THE JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 22, No. 8

August, 1952

A publication of the Academy of Sciences of the U.S.S.R.

IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU

152 West 42nd Street
New York 18, N.Y.

Printed in Great Britain

Annual Subscription $95.00
Single issue 12.00

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In subsequent investigations V. V. Chelintsev showed that the action of ethers, sulfides and tertiary amines on certain organomagnesium compounds (presenting the appearance of a snow-white solid mass) suspended in benzene leads to conversion of the organomagnesium compounds into complexes soluble in excess of the added substances. Vladimir Vasilevich thereby demonstrated that certain organomagnesium compounds are converted into oxonium, thionium and ammonium complexes. He then carried out, in the celebrated thermochemical laboratory of V. F. Luginin, careful investigations of the heat of formation of the above-mentioned compounds and of the heat of decomposition of the final complexes with water.

These determinations supplied the first data for the relative thermal effects of the formation of oxonium, thionium and ammonium complexes and for the influence of organic radicals on these magnitudes. In these researches he moved on to a new field of immense importance, namely the higher valences of organic compounds containing oxygen, nitrogen and sulfur. Pursuing his investigations in this direction, V. V. Chelintsev extended them to all classes of organic compounds — alcohols, ethers, phenols, ketones, esters, etc. His many investigations, which attracted general attention for their fundamental character and novel content, enabled him to show that these higher valences varied in dependence on the different functional groups in organic compounds. In the opinion of Academician A. E. Favorsky, these were classical investigations in the field of the oxonium compounds.

On the basis of the thermochemical investigations, V. V. Chelintsev was able to correct the earlier formulas of complex oxonium compounds, for example that of dimethylpyrrole advanced by Collis, Bayer, Villiger and others. These studies yielded a complete table of the thermochemical data relating to higher valences in all the basic groups of organic compounds. On the basis of this table we can now fairly readily predict which of these substances will displace other compounds from complexes during their interaction; the table also supplies information on the effect on these transformations of functional groups, organic radicals, and other substituents.

After studying organomagnesium compounds under laboratory conditions, V. V. Chelintsev went over to the study of such compounds in nature — in the field of chlorophyll. Here he threw light upon a series of problems; firstly, the position of magnesium in the pyrrole rings and the significance of this grouping; secondly, the configuration of the complex chlorophyll molecule with reference to the appearance in nature of a system containing four pyrrole rings in spite of the fact that two rings would have sufficed for the absorption of carbon dioxide; thirdly, the chemistry of assimilation. For these objectives he synthesized a series of magnesium-substituted pyrroles, worked out a series of new methods, and obtained such new compounds as pyrrole glycols and pyrroledicarboxylic acids. These investigations were fruitful for pyrrole chemistry in general.

In attempting to solve the second problem of the configuration of the complex chlorophyll molecule, V. V. Chelintsev investigated the condensation of pyrrole with acetone and showed that the pyrrole ring has an innate tendency to form those tetranuclear complex systems on which chlorophyll is based, and that the condensation of two-ring systems is inevitably followed by transformation into tetranuclear systems. In this manner he solved the problem of the formation in nature (in chlorophyll) of complex groupings of pyrrole rings.

Concerning the third problem — the mechanism of absorption of carbon dioxide during assimilation and its subsequent reduction — V. V. Chelintsev was not satisfied with Willstatter's scheme involving participation of the magnesium-substituted chlorophyll rings. V. V. obtained substituted acids by reacting carbon dioxide with such magnesium-substituted simplest pyrrole derivatives, and no reduction of the carbon dioxide was observed. He himself proposed a mechanism for the reaction of carbon dioxide with water under the influence of chlorophyll followed by formation of sugar.

From 1930 V. V. Chelintsev devoted his energy to the study of furan compounds and their condensations. He worked out a special method for isolating furfural from the products of distillation during the manufacture of furfural from vegetable materials. He examined the colored compounds prepared by condensing furfural with various organic compounds. On the basis of these coloring matters he and his students developed methods of determination of small amounts of acetone, furfural, formaldehyde and acetaldehyde. The work of V. V. Chelintsev on the preparation of alcohols and ketones of the furan series has considerably widened our knowledge of the chemistry of furan compounds.

V. V. Chelintsev realized a series of new syntheses also in other branches of organic chemistry: The synthesis of α-keto acids with the aid of copper cyanide; the synthesis of chalconogenic ketones; the synthesis of isomeric ketones and of unsaturated ketones with the help of magnesium-substituted aminates; the synthesis

of new crystalline complexes of ketones and esters with acids, phenols, and quinones. These investigations signposted new synthetic routes and stimulated a whole series of new researches and new ideas which left their mark in the Russian and foreign scientific literature.

V. V. Chelintsev was a member of several chemical societies. In 1933 he was chosen as corresponding member of the Academy of Sciences of the USSR, and in 1935 he was raised to the rank of "distinguished scientist".

V. V. Chelintsev was an outstanding teacher. He lectured on inorganic and organic chemistry, on chemical methodics and on the history of chemistry for over 40 years in the university and the teachers' training college. His lectures were always carefully thought out and brilliant in form. They were simple, clear, correlated with the development of the problems discussed, and were always accompanied by a series of striking experiments. They were also attended by students in other courses as well as by teachers who wished to learn how to clarify chemical problems and to perform experiments. Vladimir Vasilevich loved chemistry and had an instinct for the experimental side.

V. V. Chelintsev was a great patriot. He understood the necessity of popularizing knowledge, of making propaganda for science and of popularizing it among the vast masses. He wrote a series of books in popular language under the titles of "Organic chemistry and biographies of its outstanding figures", "Fundamental chemical concepts, laws and theories in popular presentation", "Rivalry between the laboratory and nature", "The centenary of the birth of Louis Pasteur", etc. He organized the Saratov Chemical Society and the Saratov Teachers' Naturalist Society and served them faithfully and incessantly. With his feverish energy and inexhaustible initiative, Chelintsev interested himself passionately in the problems of the chemical industry, in the development and exploitation of the natural resources of the country and in particular of his native region of Privolzh. He prepared reports for special industrial conferences in diverse national committees and in the Academy of Sciences with reference to the development of the natural wealth of the country.

Over a period of many years V. V. Chelintsev acted as consultant and fellow-worker of the Saratov "kraisovnarkhoz". He published numerous papers on the mineral and vegetable wealth of the region and undertook in the university laboratory many investigations of specimens of raw materials from different parts of the Volga Province and other regions. He was interested in petroleum, peat, shale, gases, salts, clays, pyrites and sands. He was interested in such industries as drying oils, glues, tanning agents, and hydrogenation of fats. He entered all these fields as a penetrating researcher, as a great patriot, as a pioneer in problems of technology, and as an industrial organizer.

The Government of the USSR showed high appreciation of the services of Vladimir Vasilevich Chelintsev. He was twice awarded the "Red Banner of Labor" and received a medal "for valiant service in the Great Patriotic War".

Vladimir Vasilevich devoted all his energies to the organization and prosperity of the beloved university of his native town and to the development of the natural resources of his region. He always expressed himself an enthusiastic believer in the possibilities of development of the chemical industry of the Volga Province and showed keen interest in the development of culture in Saratov, the town in which N. G. Chernyshevsky (of whom Chelintsev liked so often to talk) was born and died.

In V. V. Chelintsev Soviet chemistry has lost an outstanding scientist, a richly endowed investigator with a wide range of scientific interests who devoted all his knowledge, skill and energy to the service of the country and science. The death of Chelintsev was felt in particular by his pupils, whose link with him was never broken up to the last days, and also by Saratov University where he worked from its foundation.

The luminous figure of Chelintsev – teacher and friend – will always remain in the recollection of his pupils and comrades, while his achievements will serve for many long years as an example to fresh generations of investigators and will occupy one of the most honored places in the history of organic chemistry. His pupils will exert every effort to compensate for this heavy loss and together with the whole army of Soviet chemists they will pursue the extensive development of chemical science for the glory of our socialist state.

THE MOST IMPORTANT PUBLICATIONS OF V. V. CHELINTSEV*

I. Papers in Scientific Journals

[1] The action of isopropyl iodide on magnesium. J. Russ. Chem. Soc. 36, 549 (1904).

* The list does not include about 200 publications in separate brochures, popular editions, newspapers and special magazines on questions of chemical history, chemical industry (with particular reference to the Saratov oblast and the Volga Province), the teaching of chemistry, etc.

[2] The analogy between organic oxygen and nitrogen compounds. J. Russ. Chem. Soc. 36, 1268 (1904).

[3] The theory of the Grignard reaction and a new method of preparation of organomagnesium compounds. J. Russ. Chem. Soc. 37, 367 (1905).

[4] Transformations of some organomagnesium compounds into Grignard-Bayer oxonium bases and the thermochemical investigation of this reaction. J. Russ. Chem. Soc. 37, 1100 (1905).

[5] Concerning a new series of ether complexes of organomagnesium compounds. J. Russ. Chem. Soc. 38, 579 (1906).

[6] The problem of preparation of some organomagnesium compounds and their properties. Chem.-Zeitung, 30, 378 (1906).

[7] Thermochemical examination of the decomposition of organomagnesium-ether complexes with water. J. Russ. Chem. Soc. 38, 962 (1906).

[8] Thermochemical examination of the decomposition of some mixed organomagnesium compounds with water. Ber. 39, 1682 (1906).

[9] Heat of formation of some halogenated organomagnesium compounds from the elements and the heat of their preparation from halogenated organic compounds and magnesium. J. Russ. Chem. Soc. 38, 975 (1906).

[10] Investigation of the influence of radicals upon the character of the secondary valences of oxygen. J. Russ. Chem. Soc. 39, 1015 (1907).

[11] Investigation of cases of isomerism of Grignard and Bayer oxonium compounds. J. Russ. Chem. Soc. 39, 1019 (1907).

[12] Conversion of some organomagnesium compounds into amine complexes and their thermochemical examination. J. Russ. Chem. Soc. 39, 1250 (1907).

[13] Reciprocal transformations of magnesium-ammonium and magnesium-oxonium compounds. J. Russ. Chem. Soc. 40, 569 (1908).

[14] Oxonium dibromides of ethers and their structure. J. Russ. Chem. Soc. 41, 131 (1909). (In collaboration with V. Konovalova).

[15] Influence of the masses of reacting substances upon the formation of oxonium dibromides in various organic solvents. J. Russ. Chem. Soc. 43, 620 (1911). (In collaboration with V. Konovalova).

[16] Influence of the concentration of reacting substances upon the formation of oxonium dibromides in different organic solvents. J. Russ. Chem. Soc. 43, 633 (1911). (In collaboration with V. Konovalova).

[17] Thionium dibromides of sulfides. J. Russ. Chem. Soc. 44, 1885 (1912).

[18] Ammonium dibromides of tertiary amines. J. Russ. Chem. Soc. 44, 1894 (1912).

[19] Rate of formation of oxonium dibromides in various organic solvents. J. Russ. Chem. Soc. 44, 865 (1912).

[20] Thionium dibromides of sulfides. J. Russ. Chem. Soc. 44, 1885 (1912).

[21] Concerning the relation of organomagnesium compounds to aromatic ethers. J. Russ. Chem. Soc. 45, 289 (1913). (In collaboration with B. Pavlov).

[22] Investigation of the higher valences of oxygen-containing organic compounds. J. Russ. Chem. Soc. 45, 844 (1913).

[23] Investigation of the higher valences of oxygen-containing organic compounds. Oxonium compounds of phenol. J. Russ. Chem. Soc. 45, 864 (1913).

[24] Concerning the structure of organomagnesium complexes and the mechanism of their formation. J. prak. Chem. (2), 89, 86 (1913).

[25] Products of reaction of bromine with ethers. The compounds of Schutzenberger, Mackintosh and Chelintsev. J. Russ. Chem. Soc. 45, 1845 (1913).

[26] Investigation of the higher valences of oxygen-containing organic compounds. III. The basic properties of oxygen in aromatic alcohols. J. Russ. Chem. Soc. 45, 1909 (1913).

[27] Investigation of the higher valences of organic oxygen-containing compounds. IV. The basic properties of oxygen in alcohols of the terpene series. J. Russ. Chem. Soc. 45, 1912 (1913).

[28] Investigation of the higher valences of organic oxygen-containing compounds. V. The differences between principal and secondary values in alcohols. J. Russ. Chem. Soc. 45, 1917 (1913).

[29] The action of esters on pyrrole magnesium dibromide. Ber. 47, 2647 (1914). (With A. P. Terentyev).

[30] A new method of preparation of α-pyrrolealdehyde. Ber. 47, 2652 (1914) (With A. P. Terentyev).

[31] Investigations of the higher valences of organic oxygen-containing compounds. VI. The basic properties of oxygen in ethers. J. Russ. Chem. Soc. 46, 889 (1914).

[32] The action of esters on pyrrole magnesium bromide. J. Russ. Chem. Soc. 46, 1399 (1914). (With A. P. Terentyev)

[33] Complex magnesium compounds of pyrrole, indole and carbazole in their relations to chlorophyll. J. Russ. Chem. Soc. 46, 1876 (1914). (With B. Tronov).

[34] Magnesium derivatives of piperidine, tetrahydroquinoline and hydroacridine in the light of the theory clarifying the relative complex-forming abilities of these compounds. J. Russ. Chem. Soc. 46, 1886 (1914). (With B. Tronov).

[35] A method for preparation of dipyrrole ketone. J. Russ. Chem. Soc. 47, 170 (1915). (With D. Skvortsov).

[36] On the isomerizations of organometallic compounds of pyrrole under the action of ethyl carbonate and ethyl chlorocarbonate. J. Russ. Chem. Soc. 47, 170 (1915). (With S. Karmanov).

[37] On the nature and structure of tripyrrole. J. Russ. Chem. Soc. 47, 1224 (1915). (With B. Tronov and B. Voskresensky).

[38] Preparation of dipyrryldiphenylmethane, pyrryldiphenylcarbinol and new dyestuffs of the pyrrole series. J. Russ. Chem. Soc. 47, 1211 (1915). (With B. Tronov and A. Terentyev)

[39] The process of condensation of pyrrole with acetone. J. Russ. Chem. Soc. 48, 105 (1916). (With B. V. Tronov).

[40] The structure of the pyrrole – acetone condensation product. J.Russ.Chem.Soc., 48, 105 (1916). (with B.V.Maksorov).

[41] The condensation of pyrrole and methylpyrrole with formaldehyde and the preparation of glycols of the pyrrole series. J. Russ. Chem. Soc. 48, 748 (1916). (With B. V. Maksorov).

[42] A new method of preparation of α,α'-pyroledicarboxylic acid. J. Russ. Chem. Soc. 48, 779 (1916). (With B. V. Maksorov).

[43] Experiments on the simple condensation of pyrrole with methylethyl ketone and methylhexyl ketone; mixed condensations with acetone and methylethyl ketone and their value for establishing the formulas of chlorophyll and hemin. J. Russ. Chem. Soc. 48, 1197 (1916). (With B. V. Tronov).

[44] Experiments on the simple condensation of pyrrole with cyclohexanone and other cyclic ketones; experiments on mixed condensation with acetone and cyclohexanone and the ability of various ketones to condense with pyrrole. J. Russ. Chem. Soc. 48, 1210 (1916). (With B. V. Tronov and S. G. Karmanov).

[45] Acidic compounds. Investigation of the relative stability of the higher valence of oxygen in various classes of organic compounds. Bull. Soc. Chim. (4), 35, 741 (1924).

[46] The higher valences of oxonium compounds. Bull. Soc. Chim. (4), 37, 176 (1924).

[47] Preparation and properties of pyrrole-N-carboxylic acid and of its amides, pyrrolides and glycerol derivatives. Ber. 60, 194 (1927) (with B. Maksorov).

[48] The separation of ketones with the help of their oxonium complexes. Bull. Soc. Chim. (4), 41, 805 (1927). (With L. Nazarov).

[49] A new method of preparation of α-keto acids. Ber. 62, 2210 (1929). (With V. Schmidt).

[50] Condensations of furan derivatives. I. Secondary reactions of furfurylidene acetone with other products of acetone condensation. J. Gen. Chem. 2, 224 (1932). (With E. K. Nikitin).

[51] Study of the reaction of diethyloxalate with phosphorus pentabromide without pressure and under pressure. J. Gen. Chem. 2, 217 (1932). (With V. I. Esafov)

[52] Condensations of furan derivatives. II. Colored compounds of the furylallene series and the determination of small amounts of acetone. J. Gen. Chem. 3, 319 (1933). (With E. K. Nikitin).

[53] Condensations of furan derivatives. III. Preparation of products of condensation of furfural with acetone in acid and alkaline solutions and the determination of small amounts of acetone. J. Gen. Chem. 4, 438 (1934). (With E. K. Nikitin).

[54] Condensations of furan compounds. IV. The nature of the color of the products of condensation of furfural with acetone in sulfuric or hydrochloric acid and the theory of the reactions of alcohols and olefins with furfural. J. Gen. Chem. 5, 256 (1935). (With E. K. Nikitin).

[55] Condensations of furan compounds. V. Application of the furfurylidene method to the study of the condensation of acetone with formaldehyde. J. Gen. Chem. 5, 265 (1935). (With M. N. Tilichenko).

[56] Oxonium compounds. Acidic oxonium complexes of oxygen-containing organic compounds. Proc. Acad. Sci. USSR, 4, 304 (1934).

[57] Oxonium compounds. Proc. Acad. Sci. USSR 2, 244 (1935).

[58] On the theory of the double bond. Bull. Soc. Chim. (5), 3, 1035 (1936).

[59] Oxonium compounds. Complexes of quinone with hydrochloric, phosphoric and acetic acids and their chlorination. Proc. Acad. Sci. USSR, 14, 289 (1937).

[60] Clarification of nuclear arrangement and of the inclination of rows of molecules in layers of organic acids on the basis of X-ray diagrams. Proc. Acad.Sci. USSR, 16, 95 (1937).

[61] The structure of organomagnesium complexes. Proc. Acad. Sci. USSR, 14, 336 (1937).

[62] Preparation of alcohols of the furan series with the help of ethers and some organomagnesium compounds and their transformation into unsaturated substances and resins. J. Gen. Chem. 7, 1515 (1937). (With A. S. Larionov).

[63] Displacement of furfural by aldehydes from furfurylidene compounds as a means of determination of the concentration of formaldehyde and acetaldehyde. J. Gen. Chem. 7, 2324 (1937). (With E. K. Nikitin).

[64] The eutectics of ketone-phenol systems and the establishment with their help of the distectic points of their oxonium complexes as exemplified by monofurfurylidene acetone and dibenzylidene acetone. J. Gen. Chem. 9, 160 (1939). (With V. I. Kuznetsov and G. I. Kuznetsova).

[65] Furan systems of the chalcone type. Bull. Soc. Chim. (5) 6, 70 (1939).

[66] Condensations of furan derivatives. XI. Aliphatic and furanic diketones and their polymerization. J. Gen. Chem. 9, 1858 (1939). (With G. I. Kuznetsov).

[67] Condensations of furan derivatives. XII. Polyene compounds of the aliphatic and furanic series and their condensations. J. Gen. Chem. 9, 1901 (1939). (With G.I.Kuznetsov).

[68] Condensations of furan compounds. XIII. Displacement of aldehydes by other aldehydes from carbonyl ethylene compounds. J. Gen. Chem. 10, 1453 (1940). (With E.K.Nikitin).

[69] New petroleums of the Volga Basin. Proc. Acad. Sci. USSR, 23, 641 (1939).

[70] New petroleums of the Volga Basin and their multistage oxidative cracking in the vapor phase. Proc. Acad. Sci. USSR 26, 354 (1940),

[71] New petroleums of the Volga Basin (Second Baku). Buguruslansk petroleum and its oxidative cracking in the vapor phase. Proc. Acad. Sci. USSR 30, 144 (1941).

[72] New petroleums of the Volga Basin (Second Baku). Novo-Stepanovsk petroleum and its oxidative cracking in the vapor phase. Proc. Acad. Sci. USSR, 30, 148 (1941).

II. Monographs and Educational Accessories

[73] Some organomagnesium compounds and their transformations into ammonium and oxonium complexes. Moscow Univ. (1908).

[74] Investigation of the higher atomicities of organic compounds of oxygen, sulfur and nitrogen. Moscow Univ. (1912).

[75] Effect of the medium upon the course of chemical reactions. Saratov Univ. (1910).

[76] Outstanding features of the development of the chemistry of pyrrole compounds. Moscow Univ. (1929).

[77] Five-membered heterocyclic systems, their character and peculiarities. Moscow Univ. (1929).

[78] Chlorophyll and hemin and their related natural pigments. Saratov Univ. (1929).

[79] Contact-catalytic processes in the field of organic compounds and their application in industry. State Technical Press (1927).

[80] Organic catalysts. Acad. Sci. Press (1939).

[81] Fundamental chemical concepts, laws and theories. A treatise on the fundamental chemical concepts. Moscow. "Science" Press (1912).

[82] Organic chemistry. A textbook for students of universities and special educational institutions. Saratov (1924).

[83] Prologomena. An introduction to the study of organic chemistry. Saratov (1924).

[84] Bulletin of Russian chemical literature. Journal index of chemical literature in all branches of chemistry. Moscow (1924).

[85] Organic chemistry for technical schools. State Sci.-Tech. Institute (1931).

[86] The competition between the laboratory and nature in the organic chemical manufacturing industry, Moscow-Leningrad. State Press (1927).

THE SOLUBILITY OF CALCIUM MOLYBDATE

Vikt.I.Spitsyn and I.A.Savich

Precipitation of calcium molybdate is utilized in analytical chemistry for the quantitative determination of molybdenum [1] and calcium [2] and for separation of the latter from magnesium [3]. A number of authors have proposed to separate molybdenum in the form of calcium molybdate from industrial solutions during the processing of molybdenum ores [4,5]. However, the literature contains very little information about the solubility of calcium molybdate. According to Smith and Bradbury [1] this compound is partially soluble in water and insoluble in alcohol. Dittler [6] measured the solubility of calcium molybdate in water at temperatures of 30° and 170°. In the latter case a saturated solution was obtained at high pressure. The solubility on a molybdenum basis was (per 100 ml water) 0.0055 g at 30° and 0 0328 gat 170°. Bashilov and Kindyakov [5] determined the solubility of calcium molybdate in water at a temperature of 18° and obtained a value of 0.017 g per 100 ml (likewise calculated as molybdenum).

We have studied the solubility of calcium molybdate in water by gravimetric and colorimetric methods at various temperatures between 0° and 100°.

I. Preparation and Analysis of Normal Calcium Molybdate

Calcium molybdate was prepared by reacting (at room temperature) solutions of sodium molybdate and calcium chloride containing equimolecular amounts of these substances. The precipitate was washed for a prolonged period with water by the decantation method until chlorine ions had been completely removed. Washing was continued as long as the turbidity, developed after addition of silver nitrate to a sample, did not begin to dissolve completely in dilute nitric acid. The precipitate was drained on a Buchner funnel and dried in the air at room temperature.

The water content of the preparation was determined by calcination at 500° to constant weight, and the mean value found was 4.87% (the hemihydrate, $CaMoO_4 \cdot 0.5H_2O$, corresponds to 4.30%). Consequently our air-dried preparation approximates to the hemihydrate. The slightly high water content may be explained by the fine dispersion of the precipitate and its large surface, in consequence of which it heavily adsorbs water. The calcined preparation was analyzed for its content of calcium and molybdenum.

For the determination of calcium, about 0.2 g (exactly weighed) of the molybdate was dissolved in 20 ml of 35% hydrochloric acid, and calcium oxalate was precipitated from the solution by the usual method. Since it is more convenient in the final stage to weigh calcium sulfate rather than calcium oxide, the calcium oxide resulting from the calcination of the oxalate was moistened with water and then worked up with a few drops of conc. sulfuric acid. The mixture was evaporated to dryness and then calcined at a temperature of 500-600°.

For the determination of molybdenum the weighed sample (of the order of 0.1 g) was dissolved in sulfuric acid and precipitation was effected with α-benzoin oxime [7]. The precipitate was converted into molybdic anhydride by calcination at 500° and weighed.

The analytical results are presented in Table 1.

TABLE 1
Analysis of Calcium Molybdate

	CaO (%)	MoO_3 (%)
Found content...	28.03	71.94
	28.00	71.96
Mean	28.01	71.95
Calculated for $CaMoO_4$. . .	28.04	71.96

The contents of calcium oxide and molybdic anhydride in the preparation are close to the theoretical.

2 Study of the Solubility of Calcium Molybdate in Water by the Gravimetric and Colorimetric Methods

We investigated the solubility of calcium molybdate at temperatures of 0, 22, 50, 65, 75, 80, 90 and 100°.

Experiments in the temperature range of 22-90° were performed in a glass test-tube with a spiral stirrer and an oil seal for protection of the solution against evaporation and entry of dust from the air. 75 ml distilled water was introduced into the test-tube followed

by a weighed amount of about 0.4 g calcium molybdate. The test tube was placed in a thermostat whose temperature was kept constant by means of an electric heater with a contact thermometer. The temperature was observed to fluctuate in the range of ± 0.5°. Observations at 0° were made with the thermostat filled with snow and water. The mixing of the liquid with the calcium molybdate was usually effected continuously over a period of several days.

The determination of solubility at 100° was performed with the help of a 1-liter flask fitted with a 12-bulb reflux condenser. The flask contained 750 ml distilled water and 4 g calcium molybdate. Boiling was continued for 48 hours in order to establish equilibrium. In these experiments the temperature variations were likewise within the limits of ± 0.5°.

Samples of the solution were withdrawn with glass pipets whose ground-glass tips contained a filter plate of porous glass. A small piece of cotton wool was also placed beneath the filter. The pipet was wrapped in cotton wool to guard the solution against changes of temperature. Establishment of equilibrium was checked with the help of control samples which were analyzed colorimetrically for their molybdenum content.

The molybdenum was determined colorimetrically by Chernikov's method [8], involving the formation of a colored complex of the composition (according to Babko [9]) $Mo(CNS)_5$. A Duboscq colorimeter was used for comparing the color intensities.

Gravimetric determination of the solubility was carried out when the concentration of molybdenum in the liquid phase had become constant. A sample of the solution was transferred to a weighing bottle. The weight of the solution was found and then evaporation was performed in a drying cupboard. The solid residue was brought to a constant weight at 200°. A determination was also made of the content of anhydrous salt in 100 g of solution. The minute amount of adsorbed water remaining in the preparation after drying under the stated conditions does not exceed 0.1% and may be ignored. The solubility of calcium molybdate in 100 ml of solution was determined colorimetrically. The experimental data are presented in Tables 2 and 3 and plotted in the diagram.

TABLE 2

Solubility of Calcium Molybdate (Method of evaporation of solution)

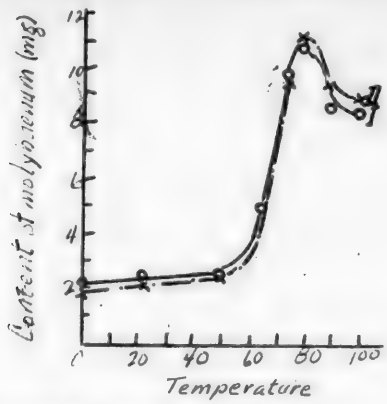
Temp.	Expt. No.	Wt. of solution, g	Wt. of dry residue	Amount of dry substance in 100 g of solution	Mean, g	Molybdenum content of 100 g of solution	Solubility of the salt in moles/100 g solution
0°	1	25.93	0.0012	0.0046	0.0046	0.0022	$2.3 \cdot 10^{-4}$
	2	23.45	0.0011	0.0046			
22	1	19.82	0.0010	0.0052	0.0052	0.0025	$2.6 \cdot 10^{-4}$
	2	21.67	0.0012	0.0052			
50	1	19.63	0.0011	0.0057	0.0056	0.0027	$2.8 \cdot 10^{-4}$
	2	17.98	0.0010	0.0056			
65	1	52.27	0.0052	0.0099	0.0102	0.0049	$5.1 \cdot 10^{-4}$
	2	56.13	0.0060	0.0106			
75	1	51.53	0.0106	0.0205	0.0204	0.0098	$1.2 \cdot 10^{-3}$
	2	31.49	0.0063	0.0203			
80	1	39.56	0.0089	0.0226	0.0227	0.0109	$1.13 \cdot 10^{-3}$
	2	29.39	0.0067	0.0229			
90	1	52.73	0.0093	0.0177	0.0178	0.0087	$8.9 \cdot 10^{-4}$
	2	56.86	0.0102	0.0179			
100	1	40.77	0.0072	0.0176	0.0177	0.0085	$8.8 \cdot 10^{-4}$
	2	53.77	0.0096	0.0178			

TABLE 3

Content of Molybdenum in 100 ml of Saturated Solution of Calcium Molybdate (Colorimetric Method)

Temperature	0°	22°	50°	75°	80°	90°	100°
Content of molybdenum in 100 ml solution (g)	0.0019	0.0022	0.0025	0.0095	0.0112	0.0095	0.0090
Solubility of the salt (in moles per liter)	$2.0 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$9.9 \cdot 10^{-4}$	$1.16 \cdot 10^{-3}$	$9.9 \cdot 10^{-4}$	$9.4 \cdot 10^{-4}$

The analyses of the solid phase from the experiments on determination of the solubility of calcium molybdate showed that its composition did not differ from that of the starting preparation. It can therefore be concluded that no hydrolytic processes took place during the action of water on the calcium molybdate.



Solubility of calcium molybdate at various temperatures. I) Molybdenum content (by gravimetric method) in mg/100 g solution. II) Molybdenum content (by colorimetric method) in mg/100 ml solution.

The mean accuracy of the colorimetric determination of molybdenum for the given concentrations is 5-10%. We can therefore consider the agreement between the colorimetric method and the evaporation method to be quite satisfactory. Attention may be drawn to the higher values in the literature for the solubility of calcium molybdate in water at around room temperature.

The data of Tables 2 and 3 (see also the diagram) indicate that the solubility of calcium molybdate increases continuously from 0 to 80° and then declines. In this behavior calcium molybdate is reminiscent of gypsum whose solubility curve passes through a maximum at 38°. We are of the opinion, however, that in the case of calcium molybdate the inflection point on the solubility curve corresponds to a change in the hydrated state of the salt.

SUMMARY

1. The solubility in water of normal calcium molybdate was investigated over the temperature range of 0-100°.

2. Colorimetric determination of the molybdenum content and determination by the method of evaporation of saturated solutions of calcium molybdate gave results in close agreement.

3. The solubility curve of calcium molybdate is characterized by an inflection point (maximum) at a temperature of 80°.

LITERATURE CITED

[1] E. F. Smith, R. H. Bradbury, Ber. 24, 2930 (1891).

[2] A. B. Burevich and N. V. Lokhonova, Factory Labs 110 (1934).

[3] R. Willy, Ind. Eng. Chem., 3, 2 (1931).

[4] J. P. Bonardi, Chem. Met. Eng. 21, 367 (1919); E. Pokorny, German Patent 588564.

[5] I. Ya. Bashilov and P. S. Kindyakov, Non-Ferrous Metals USSR, 1931, no. 7, p. 879.

[6] E. Dittler, Z. Kryst. 54, 332 (1915).

[7] H. B. Knowles, Bur. of Stand., J. of Research 9, 1 (1932); I. M. Kolthoff and E. B. Sandell, Quantitative Analysis, State Sci.-Tech. Institute, 650 (1938).

[8] See Berl-Lunge, Physical Methods of Chemical Analysis, Vol. II, Part 2, no. 2, State Sci.-Tech. Institute, 250 (1938).

[9] A. K. Babko, J. Gen. Chem. USSR, 17, 642 (1947).

Received December 19, 1950

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INVESTIGATION OF THE MIXED SULFATES OF THE ALKALI ELEMENTS AND AMMONIUM

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There are very few data in the literature on the preparation of mixed sulfates of the alkali elements and ammonium. Troost [1] points out that reaction of solutions of the normal sulfates of lithium and ammonium followed by evaporation yields the lithium-ammonium sulfate $Li_2SO_4 \cdot (NH_4)_2SO_4$. No information is available about the behavior of such compounds when heated.

In this research we have investigated the conditions of preparation of mixed sulfates of all of the alkali metals and ammonium, and also the thermal stability of these compounds.

The starting materials for the preparation of the compounds were the pyrosulfates of the alkali elements which we described previously [2]. Weighed amounts of the pyrosulfates in procelain crucibles were dissolved in small amounts of water; the solutions were treated with concentrated ammonia and left to evaporate in desiccators over phosphorus pentoxide. After a few days crystallization of the salts commenced. The crucibles with their contents were removed from the desiccators and crystallization was completed in the air over a period of 9-10 days.

TABLE 1

Analysis of the Mixed Sulfates of the Alkali Elements and Ammonium

Compound	SO_3 content, %	
	found	calculated
$LiNH_4SO_4$	66.22	66.14
$NaNH_4SO_4$	58.32	58.40
KNH_4SO_4	52.59	52.26
$RbNH_4SO_4$	40.23	40.11
$CsNH_4SO_4$	32.38	32.41

Determinations of the SO_3 content (and in some cases of the NH_3) were carried out by the usual methods on the air-dry crystals. All of the isolated salts had a composition represented by the formula $MeNH_4SO_4$, where Me is an alkali element. See Table 1 for the analytical results.

In the mixed rubidium-ammonium sulfate the ammonia content was also determined and was found to be 8.25%, as compared with 8.51% for $RbNH_4SO_4$.

The structure of the compounds remains unclarified since the data agree equally well with the formulas $MeNH_4SO_4$ and $Me_2SO_4 \cdot (NH_4)_2SO_4$.

If we assume the first formula to be the more probable, we may express the formation reaction by the following equations:

$$Me_2S_2O_7 + H_2O = 2MeHSO_4; \quad MeHSO_4 + NH_3 = MeNH_4SO_4.$$

In Figure 1 is a photograph of the lamellar crystals of cesium-ammonium sulfate which readily aggregate into large concretions. (See plate p. 1521).

The thermal stability of the mixed sulfates was investigated by heating weighed amounts in porcelain crucibles in a drying cupboard or in an electric furnace until constant in weight. Analyses of the final products showed that these were always the pyrosulfates.

The decomposition of the mixed sulfates evidently proceeds according to the equation:

$$2MeNH_4SO_4 = Me_2S_2O_7 + 2NH_3 + H_2O.$$

We did not observe the formation of hydrosulfates as intermediate products.

In Table 2 are detailed the start of conversion of the mixed sulfates into pyrosulfates, the yield of the latter, and the experimental and theoretical contents of SO_3 in the products obtained. These data indicate that the thermal stability of the mixed sulfates of the alkali elements and ammonium increases in passing from lithium to cesium. The potassium-ammonium and rubidium-ammonium sulfates have similar decomposition temperatures. The most

TABLE 2

Heating of the Mixed Sulfates of the Alkali Elements and Ammonium

Compound	Initial temp. of conversion to pyrosulfate	Yield of $Me_2S_2O_7$ from $MeNH_4SO_4$ (in % of theory)	% SO_3 content in the final product	
			found	calcd. for $Me_2S_2O_7$
$LiNH_4SO_4$	100-130°	99.14	84.09	84.27
$NaNH_4SO_4$	150-170	98.59	72.03	72.09
KNH_4SO_4	170-190	100.39	62.59	62.96
$RbNH_4SO_4$	170-200	99.31	46.04	46.14
$CsNH_4SO_4$	270-300	99.78	36.29	36.23

stable of the compounds prepared is cesium-ammonium sulfate.

In a previous investigation we established the thermal conditions for transformation of the hydrosulfates of the alkali metals into pyrosulfates [3]. It may be noted that for the sulfates of lithium-ammonium, sodium-ammonium and potassium-ammonium the temperature of initial decomposition only exceeds by 10-20° the temperature of transition of the corresponding hydrosulfates into pyrosulfates, while in the case of rubidium-ammonium sulfate and rubidium hydrosulfate these temperatures coincide. By contrast, cesium-ammonium sulfate decomposes at a temperature 120° higher than the decomposition temperature of the corresponding hydrosulfate.

In all cases the decomposition temperatures of the mixed sulfates lie considerably below the temperatures of initiation of transformation of the pyrosulfates into the normal sulfates. Consequently the addition of ammonia to pyrosulfates fails to facilitate the process of transformation of the latter into normal sulfate by heating.

Just as in the case of hydrosulfates [3], the stability of the investigated mixed sulfates is observed to increase with increasing atomic number of the alkali elements. This is clearly bound up with the reduced polarizing action of cations with increase in their radii, which leads to weakening of the contrapolarization in HSO_4^{-2} or $NH_4SO_4^{-2}$ ions.

It is interesting to note that the addition of ammonia to the HSO_4^{-1} ion has no marked effect upon the thermal stability of the compound. We may conclude that the bonding of hydrogen with the SO_4^{-2} ion has the same effect upon the properties of the mixed sulfate as it has upon the properties of the hydrosulfate.

SUMMARY

1. Mixed sulfates of all of the alkali elements and ammonium of the general composition $MeNH_4SO_4$ were prepared by crystallization of ammoniacal solutions of pyrosulfates.

2. The prepared compounds decompose on heating and are transformed into the pyrosulfates.

3. The temperatures of this transformation to pyrosulfates increase with increasing ionic radius of the alkali elements and are close to the temperatures of conversion of the corresponding hydrosulfates to pyrosulfates.

LITERATURE CITED

[1] L. Troost, Ann. chim. phys. (3), 51, 132 (1857).

[2] Vikt. I. Spitsyn and M. A. Meerov, J. Gen. Chem. 22, 905 (1952); see Consultants Bureau translation, p. 963.

[3] Vikt. I. Spitsyn and M. A. Meerov, J. Gen. Chem. 22, 901 (1952); see Consultants Bureau translation, p. 959.

Received December 30, 1950

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SOME TERNARY COMPLEXES OF COPPER AND SILVER

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In recent times numerous investigations have been made of the formation and stability of so-called "ternary complexes", i.e. complex compounds containing various addenda and one and the same central ion.

A. K. Babko [1] adduced weighty evidence for the existence of such compounds in the system copper-pyridine-salicylate and studied their stability. Meites [2] detected the complexes $[Cu_2(OH)_2C_2O_4]$ and $[Cu(OH)_2Cu_2]^{2-}$ and used a polarographic method to measure their stability constants. The complexes of $[Hg_2Cl_2(C_2O_4)_2]^{2-}$ have also been formed and their stability measured [3]. Salts of copper and silver evidently possess a strong tendency to form mixed complexes. Salts of the type of $nCuX \cdot mRX \cdot R_2S_2O_3$, for example, were prepared by Rosenheim and Steinhauser [4], Canneri and Luchini [5], and others. (In the foregoing formula X is halogen or CNS^-, and R is a cation of ammonium or an alkali metal). Similar salts containing a silver cation were also prepared [4].

For the purpose of ascertaining whether ternary complexes can exist in solution, we have made a study of the solubility of CuI and CuCNS in $Na_2S_2O_3$ solution. It was conjectured that if evidence could be obtained that the reaction took place in accordance with the following scheme:

$$MX_{solid} + I^-_{aq} = MXI^-_{aq} , \qquad (I)$$

the problem would be clarified and an explanation obtained of the phenomena accompanying the solution of silver halides in potassium thiocyanate solutions [6]. Randall and Halford [6] drew attention to the futility of interpreting the results obtained with the aid of any simple assumptions.

Thiosulfate and halide complexes of silver and copper have been studied by numerous investigators. The abundance of the published material in this field makes it impossible to compile even a brief summary of the literature. We shall limit ourselves to remarking that in spite of the large number of publications devoted to thiosulfate complexes of copper, the stability constants of these complexes have never been measured. On the other hand the stability constants of the halide complexes of copper and silver, also of the thiosulfate complexes of silver, have been determined by many authors [7,8,9,10].

EXPERIMENTAL

As mentioned above, we used the solubility method to test the above hypothesis of the existence of mixed complexes in aqueous solutions.

The choice of cupric iodide and thiocyanate was dictated by their constancy of composition and their ease of preparation. Both of the compounds are formed from components in strictly stoichiometrical ratios. They were synthesized in accordance with the procedures of quantitative analysis from chemically pure reagents ($CuSO_4 \cdot 5H_2O$; KI; KCNS; and $Na_2S_2O_3 \cdot 5H_2O$.)

The prepared salts were thoroughly washed with water and introduced in the moist form into solutions of sodium thiosulfate. Solution of the solid phase was effected by continuous agitation over a period of several days until the establishment of equilibrium in the system at a temperature of $25 \pm 0.1°$. After reaching equilibrium the solutions were analyzed for their content of $S_2O_3^{2-}$ and Cu^+. Both of the ions were determined iodimetrically. The former ion was titrated immediately by the direct or reverse method (by introducing an excess of iodine and back-titrating). For determination of Cu^+ the solution was first freed from $S_2O_3^{2-}$ by heating with conc. HNO_3 and the latter was removed by evaporation with H_2SO_4. In the case of solutions with a high concentration of $S_2O_3^{2-}$ an analysis was made of the solid phase which always contained Cu and CuCNS. Results are presented in Tables 1 and 2.

EVALUATION OF RESULTS

On analyzing the compounds which they had isolated, Ryabchikov and Silnichenko [11] came to the conclusion that salts of the following types can be obtained in aqueous solutions: $Me[Cu(S_2O_3)]$, $Me_4[Cu_2(S_2O_3)_3]$ and $Me_3[Cu(S_2O_3)_2]$.

TABLE 1

Solubility of CuI in Solutions of Sodium Thiosulfate

No.	Molarity·10^2			$\frac{[Cu^+]}{[S_2O_3^{2-}]}$
	$Na_2S_2O_3$			
	Total	free	CuI	
1	1.927	0.372	1.555	4.18
2	3.624	0.844	2.780	3.29
3	4.210	0.764	3.446	4.51
4	7.029	1.759	5.270	3.00
5	7.940	1.856	6.084	3.28
6	8.708	2.054	6.654	3.24
7	18.05	4.20	13.85	3.30
8	32.54	7.51	25.03	3.33
9	44.20	10.65	33.55	3.15
10	53.76	10.94	42.82	3.91
		Mean value		3.52

TABLE 2

Solubility of CuCNS in Solutions of Sodium Thiosulfate

No.	Molarity·10^2			$\frac{[Cu^+]}{[S_2O_3^{2-}]}$ ·10
	$Na_2S_2O_3$			
	Total	free	CuCNS	
1	1.720	1.383	0.3368	2.43
2	2.109	1.690	0.4194	2.48
3	3.542	2.772	0.7705	2.78
4	4.900	3.935	0.9652	2.45
5	6.370	5.065	1.305	2.58
6	7.750	6.002	1.748	2.91
7	11.94	9.118	2.822	3.09
8	18.41	14.11	4.304	3.05
9	24.32	18.19	6.127	3.37
10	33.72	25.08	8.645	3.45
11	42.46	31.45	11.01	3.50
12	52.16	38.62	13.54	3.51
13	83.23	59.25	23.98	4.05
		Mean value		3.05

However, in a solution of copper iodide in sodium thiosulfate, ions of $CuS_2O_3^-$, $[Cu_2(S_2O_3)_3]^{4-}$ and $[Cu(S_2O_3)_2]^{3-}$ are apparently not formed. The impossibility of existence of the latter two ions follows from the fact that the formation of such complexes would necessitate the combination of 3/2 or 2 molecules of $Na_2S_2O_3$ with each ion of copper. In solution, however, the ratio $[Na_2S_2O_3]:[CuI]$ never reaches these values but always remains below 1.35.

If the dissolution of CuI in $Na_2S_2O_3$ solution had proceeded according to the scheme:

$$CuI_{solid} + S_2O_3^{2-} = CuS_2O_3^- + I^-, \qquad (II)$$

then the solubility of CuI in $Na_2S_2O_3$ would have changed proportionally to the square root of the concentration of free thiosulfate. The data of Table 1 show, however, a linear dependence. These inconsistencies can be readily eliminated if we assume that the process of dissolution of CuI in $Na_2S_2O_3$ proceeds according to the equation:

$$CuI_{solid} + S_2O_3^{2-} = [CuIS_2O_3]^{2-}, \qquad (III)$$

$K = 3.5 \pm 0.5$; $\Delta z = -742$ cal.

The calculated values of the equilibrium constant for reaction (III) are listed in Table 1. Here the value of the constant is 3.5 ± 0.5 on condition that the activity coefficients of $CuS_2O_3^-$ and $S_2O_3^{2-}$ ions are equal. On the basis of this value of the equilibrium constant we have calculated the change in thermodynamic potential (Δz).

The formation of the complex ion $[CuIS_2O_3]^{2-}$ appears to us more probable than the simultaneous existence in the solution of $CuS_2O_3^-$ and I^- ions since the latter manifest a marked tendency to enter into firm combination with Cu^+ and its independent existence is improbable.

The change in solubility detailed above might be explicable through the formation of ions of $Cu(S_2O_3)_2^{3-}$ and of CuI_2^- in equi-ionic ratios, but we are hardly entitled to assume the absence of reaction between these ions.

The equilibrium constant of reaction (III) is related to the solubility product of CuI and to the stability constant of the $[CuIS_2O_3]^{2-}$ complex by the expression:

$$K = \frac{Pr}{K_N} \qquad (1)$$

where K is the equilibrium constant of reaction (III), Pr is the solubility product of CuI, and K_N is the stability constant of the $[CuIS_2O_3]^{2-}$ complex. If we take the value of $1.1 \cdot 10^{-12}$ [13] for Pr_{CuI}, we find for K_N:

$$\frac{[Cu^+][I^-][S_2O_3^{2-}]}{[CuIS_2O_3^{2-}]} = 3.1 \cdot 10^{-12}.$$

On the basis of the above expressions we have assumed a similar solution mechanism for CuCNS:

$$CuCNS_{solid} + S_2O_3^{2-} = [Cu(CNS)S_2O_3]^{3-}. \qquad (IV)$$

$K = 0.30 \pm 0.05$; $\Delta z = 713$ cal.

The equilibrium constant for reaction (IV) is given in Table 2. It is equal to 0.30 ± 0.05. In this case, however, a small but appreciable rise in the constants is observed with increasing $Na_2S_2O_3$ concentration. We might explain this phenomenon either by inconstancy of the ratio of the activity coefficients or by the formation of complexes with a larger number of coordinated $S_2O_3^{2-}$ ions. If such complexes were indeed formed, then their concentration – judging by the magnitude of the change in the equilibrium constant – must be low.

The solubility product of CuCNS is equal to $4 \cdot 10^{-14}$ [13], and therefore the stability constant of $[Cu(CNS)S_2O_3]^{3-}$ is

$$\frac{[Cu^+][CNS^-][S_2O_3^{2-}]}{[Cu(CNS)(S_2O_3)^{2-}]} = 1.3 \cdot 10^{-12}.$$

The similarity between the stability constants of both of the ternary complexes is striking. By assuming that the formation of the ternary complexes according to scheme (I) occurs fairly frequently, we find an explanation of the hitherto puzzling data of Randall and Halford [6]. Dissolution of AgCNS in RCNS solution can only lead to formation of ions of the type of $[Ag(CNS)_n]^{1-n}$. Analysis of the data of Randall and Halford shows that the reaction in this case proceeds according to the equation:

$$AgCNS_{solid} + 3CNS^- = [Ag(CNS)_4]^{3-}. \qquad (V)$$

$K = 1.2 \pm 0.5 \cdot 10^{-1}$; $\Delta z = 1255$ cal.

The equilibrium constant of this reaction is found to be $1.2 \pm 0.5 \cdot 10^{-1}$ (Table 3).

TABLE 3

Solubility of Silver Thiocyanate in Potassium Thiocyanate Solutions

Expt. No.	Molarity $AgCNS \cdot 10^3$	KCNS total	KCNS free	free	$\frac{[AgCNS]}{[KCNS]^3} \cdot 10^2$
1	2.02	0.312	0.306	0.029	7.03
2	12.1	0.564	0.528	0.147	8.23
3	45.8	0.870	0.732	0.393	11.6
4	98.5	1.124	0.829	0.570	17.1
				Mean value	$12 \pm 5 \cdot 10^{-2}$

The solubility product of AgCNS is equal to $1.16 \cdot 10^{-12}$. Using this value we find for $[Ag(CNS)_4]^{3-}$ a stability constant of $1.0 \pm 0.5 \cdot 10^{-11}$.

This value is in good agreement with the stability constant of $Ag(CNS)_3^{2-}$, found by Ferrell and co-workers by the e.m.f. method [10]. For the $[Ag(CNS)_3]^{2-}$ complex Ferrell and co-workers found a value of $K_N = 1.7 \cdot 10^{-11}$, and for $[Ag(CNS)_2]^-$ a value of $K_N = 2.0 \cdot 10^{-11}$.

The solubility of AgI in KCNS changes linearly with the change in KCNS concentration (Table 4), as can be seen from the results of Randall and Halford. These results, however, are not distinguished by a high degree of accuracy.

In order to account for the linearity of the dependence of the solubility on the KCNS concentration, we may put forward two reaction schemes:

$$AgI_{solid} + 2CNS^- = (Ag(CNS)_2]^- + I^-; \qquad (VI)$$

$$AgI_{solid} + CNS^- = [AgICNS]^-. \qquad (VII)$$

$K = 1.2 \pm 0.7 \cdot 10^{-4}$; $\Delta z = 5345$ cal.

Scheme (VI) proposed by the authors is hardly probable on two grounds: Firstly, it is difficult to accept the possibility of displacement of iodine ions into the outer shell by the less firmly bound thiocyanate ions; secondly, the

calculation of the stability constant of $[Ag(CNS)_3]^{2-}$ according to scheme (VII) gives a value of the order of 10^{-7}, which is inconsistent with the data presented above. Calculation of the equilibrium constant of reaction (VII) leads to a value of $1.2 \pm 0.7 \cdot 10^{-4}$. The stability constant of $[AgCNS]^{-}$ calculated on this basis is equal to $7.1 \cdot 10^{-12}$ ($Pr_{AgI} = 8.5 \cdot 10^{-17}$). This result is in good accord with literature data for complexes of the $[AgX_n]^{(n-1)-}$ type with iodide and thiocyanate.

TABLE 4

Solubility of Silver Iodide in KCNS Solutions

Expt. No.	Molarity			$\frac{[Ag^+]}{[KCNS]} \cdot 10^4$
	$AgI \cdot 10^4$	KCNS		
		total	free	
1	0.20	0.202	0.202	0.99
2	0.14	0.315	0.315	0.44
3	0.67	0.425	0.425	1.57
4	0.51	0.500	0.500	1.02
5	0.40	0.608	0.608	0.66
6	0.97	0.710	0.710	1.36
7	1.46	0.765	0.765	1.91
8	1.63	1.009	1.008	1.63
		Mean value		$1.2 \pm 0.7 \cdot 10^{-4}$

S. I. Burmistrov directed our attention to the fact that in the case of dissolution of AgBr in KCNS the solid phase must be silver thiocyanate and not bromide (on the basis of the ratio of the solubility products). Our experiments showed indeed that in this case AgCNS is precipitated, so that all the data of Randall and Halford relating thereto are erroneous.

In conclusion we may point out that the fairly old data of Valents [12] on the solubility of silver halides in sodium thiosulfate solutions confirm our theory that the reactions do not proceed according to the equation:

$$AgX_{solid} + S_2O_3^{2-} = AgS_2O_3^{-} + X^{-} \qquad (VIII)$$

but according to the equation:

$$AgX_{solid} + S_2O_3^{2-} = [AgXS_2O_3]^{2-}. \qquad (IX)$$

A third possibility of formation of complexes of the type of $[Ag(S_2O_3)_2]^{3-}$ when dissolving silver chloride in sodium thiosulfate solutions is excluded by the fact that the ratio of the concentration of sodium thiosulfate to the concentration of dissolved silver chloride never reaches a value of 2.

Scheme VIII is rather improbable because the solubility changes linearly with increasing concentration of sodium thiosulfate and not in proportion to the square root of this concentration. Furthermore, the calculation of the stability constant of the $AgS_2O_3^{-}$ ion, starting from the solubility of AgCl, AgBr and AgI, leads to three different results, namely:

$$0.7 \cdot 10^{-9},\ 2.0 \cdot 10^{-12} \text{ and } 1.1 \cdot 10^{-13}.$$

Consequently all the data support the scheme IX. The equilibrium constants and the changes in free energy have the following values:

$AgCl_{solid} + S_2O_3^{2-} = AgClS_2O_3^{2-}$. $K = 2.2 \pm 0.4$; $\Delta z = -466.6$ cal.

$AgBr_{solid} + S_2O_3^{2-} = [AgBrS_2O_3]^{2-}$. $K = 0.8 \pm 0.2$; $\Delta z = 132.1$ cal.

$AgI_{solid} + S_2O_3^{2-} = [AgIS_2O_3]^{2-}$. $K = 3.2 \pm 0.2 \cdot 10^{-6}$; $\Delta z = 2038$ cal.

Below are given the stability constants calculated from the preceding data:

$$\frac{[Ag^+][Cl^-][S_2O_3^{2-}]}{[AgClS_2O_3^{2-}]} = 0.7 \cdot 10^{-10}; \quad \frac{[Ag^+][Br^-][S_2O_3^{2-}]}{[AgBrS_2O_3^{2-}]} = 4.1 \cdot 10^{-13}; \quad \frac{[Ag^+][I^-][S_2O_3^{2-}]}{[AgIS_2O_3^{2-}]} = 2.7 \cdot 10^{-13}.$$

All of the considerations put forward above support the assumption that ternary complexes are formed fairly frequently. The necessity for their investigation has been clearly revealed. We may add that in the light of the ideas here developed, great caution should be applied when making calculations of the equilibria between a precipitate and a solution containing complexing ions.

SUMMARY

1. It has been established by an analysis of our experimental data and of the data of other workers that when halides of copper (I) and silver dissolve in thiosulfate solutions, mixed complexes of the type of $[MeXS_2O_3]^{3-}$ are formed.

2. The solubility of CuI and CuCNS in thiosulfate solutions was measured at various temperatures and calculations were made of the stability constants of the resultant $[CuIS_2O_3]^{3-}$ and $[Cu(CNS)S_2O_3]^{3-}$ ions; the respective values were $3.1 \cdot 10^{-13}$ and $1.3 \cdot 10^{-13}$.

3. On the basis of literature data for the solubility of silver halides in thiocyanate and thiosulfate solutions the stability constants of the following ions were calculated: $[Ag(CNS)_4]^{3-}$, $[AgICNS]^-$, $[AgClS_2O_3]^{2-}$, $[AgBrS_2O_3]^{2-}$, $[AgIS_2O_3]^{2-}$.

LITERATURE CITED

[1] A. K. Babko, J. Gen. Chem. 18, 1607 (1948).

[2] L. Meites, J. Am. Chem. Soc. 72, 180, 184 (1950).

[3] Mei-Chio-Chen and Chi-Ju Hsiao, Chem. Abs. 38, 2895 (1944).

[4] A. Rosenheim, S. Steinhauser, Z. allg. anorg. Chem. 25, 72 (1900).

[5] G. Canneri, R. Luchini, Chem. Zentr., III, 528 (1923).

[6] M. Randall, J. Halford, J. Am. Chem. Soc. 52, 178 (1930).

[7] W. Latimer. Oxidation potentials. New York, (1938).

[8] I. M. Korenman, J. Gen. Chem. 16, 157 (1946).

[9] W. Erber, Chem. Abs. 37, 1947 (1943).

[10] E. Ferrell, J. M. Ridgton, H. L. Riley, J. Chem. Soc. 1936, 1125.

[11] D. I. Ryabchikov and V. G. Silnichenko. Bull. Acad. Sci. USSR, Div. Chem. Sci., No.1, 19 (1947).

[12] Cited by E. Cohen, Z. phys. Chem. 18, 61 (1895).

[13] Yu. Yu. Lure, Supplement to Volumetric Analysis by Kolthoff and Stenger, Vol. 1, Moscow-Leningrad, 1950.

Received December 14, 1950

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PHYSICO-CHEMICAL INVESTIGATION OF THE PHOSPHORUS TRICHLORIDE–BROMINE SYSTEM. II.

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An investigation of the PCl_3–bromine system by the method of thermal analysis [1] revealed the formation of two compounds: PCl_3Br_4 (orange-red prisms melting at 37.5°) and PCl_3Br_{18} (long cherry-red needles melting at 24.5°). Both of these compounds were obtained in the pure state. They proved to be fairly strong electrolytes; the specific electric conductivity of these complexes in the fused state at 45-65° is of the order of 10^{-4} $ohm^{-1}cm^{-1}$.

Consideration of the mechanism of formation and chemical nature of these chlorobromides of phosphorus led to the suggestion that PCl_3Br_4 and PCl_3Br_{18} are polybromides – products of addition of bromine to initially formed PCl_3Br_2. In this connection it was conjectured that in the system PCl_3–bromine may be formed not only PCl_3Br_4 and PCl_3Br_{18} but also other chlorobromides with different amounts of bromine (>4 and <18), whose existence for some reason or other was not manifested on the fusion diagram.

The aim of the present investigation was to continue the foregoing work in order to obtain a deeper insight into the characteristics of these complex compounds, and also in order to obtain further evidence for the proposed mechanism of formation and for the nature of these higher phosphorus halides.

For the purpose of determining the composition of the complex in the liquid phase the viscosity of the system PCl_3–Br_2 was studied. In addition, electrochemical investigations were made of these complexes in organic solvents.

Viscosity of the System PCl_3–Br_2

The viscosity was determined with the help of the apparatus and method described in the paper by Ya.A. Fialkov and I.D.Muzik [2] with the sole difference that all the tubes through which air passed were fitted with calcium chloride tubes since the investigated system is extremely hygroscopic.

The solutions for the viscosity measurements were prepared as follows: an exact amount of bromine was weighed into a small conical flask which could be closed with a ground-glass stopper; a 50 cc separating funnel, on which was placed a rubber stopper which formed a good fit on the flask, was weighed separately. Into this separating funnel was weighed a quantity of PCl_3 sufficient to give a solution of a definite concentration. The separating funnel was then attached to the flask with the help of the rubber stopper. The flask was stood in cold water (the reaction between PCl_3 and bromine is accompanied by considerable evolution of heat) and PCl_3 was run dropwise into the bromine. The funnel was then lifted off and the flask closed with the glass stopper. The mixture was shaken for several minutes and then transferred to the viscosimeter.

Viscosity measurements were performed at temperatures of 25 and 40°. The thermostat was a 5-liter bath filled with water. Temperature variations did not exceed $\pm 0.1°$. The liquid existed in the supercooled state at concentrations exceeding 25 mole % at 25°.

The specific gravities, required for the viscosity calculations, were determined in a pycnometer with an expansion in the upper part of the capillary. Viscosities were determined on the identical solutions whose viscosities were to be measured.

The viscosity and specific gravity data are given in Table 1 and Figure 1. On this diagram the fusibility curve of the same system is shown for comparison.

The absolute viscosity was calculated from the expression:

$$\eta = \eta_0 \frac{dt}{d_0 t_0},$$

TABLE 1

Viscosity of the System PCl_3-Br_2

PCl_3 (mole %)	η (in centipoises)		d - specific gravity	
	25°	40°	25°	40°
Br	1.305	1.131	3.118	3.065
1.31	1.439	–	3.125	–
6.24	2.345	–	3.138	–
10 45	3.458	3.269	3.142	3.123
12.21	5.882	4.147	3.145	3.112
14.31	8.491	5.608	3.128	3.096
17.07	12.722	7.508	3.066	3.032
20.03	13.061	7.719	3.032	2.997
23.49	13.015	7.580	2.961	2.924
24.71	12.624	–	2.921	–
27.22	11.058	6.329	2.846	2.809
28.92	11.014	6.371	2.850	2.815
33.33	11.734	6.793	2.874	2.839

where η_0 is the absolute viscosity of water at the temperature of measurement [3], d_0 and t_0 are the specific gravity and period of efflux of water [3], $\underline{d}$ and $\underline{t}$ are the specific gravity and period of efflux of the investigated system,

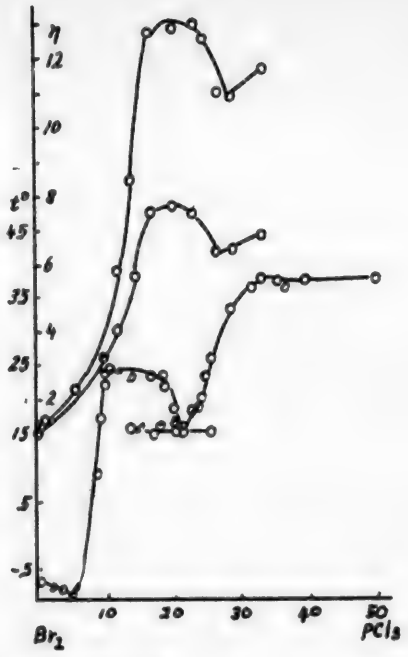

Fig. 1. Diagram of the and viscosity of the system PCl_3-Br_2

The table and diagram show that the viscosity isotherm of the system PCl_3-Br_2 is characterized by a flat maximum whose position does not change with rising temperature.

The maximum viscosity is at a concentration of 20 mole % PCl_3, which corresponds to the formation of the complex compound PCl_3Br_2.

With further rise of concentration (above 20 mole %) the viscosity isotherm at first descends smoothly and then more abruptly, reaching a minimum at 27-28 mole % PCl_3, after which it rises until the content of PCl_3 is 33 mole % and layer separation occurs [1].

The viscosity of fused PCl_3Br_4, i.e., the viscosity of the system PCl_3-Br_2 at a PCl_3 content of 33 mole %, was measured in the following manner: excess of PCl_3 was added to bromine until stratification occurred. After crystallization of the lower layer (PCl_3Br_4), the upper layer (saturated solution of PCl_3Br_4 in PCl_3 which had a constant viscosity) was poured off, and the reaction vessel (a test tube drawn out at several places) was sealed and placed in the upturned position for a period of days until the liquid was completely filled with crystals. The part of the test tube containing the crystals was detached, the crystals were fused and their viscosity measured at 25° (in the supercooled state).

Electric Conductivity of Solutions of Phosphorus Chlorobromides in Organic Solvents

It had been observed when measuring the electric conductivity of PCl_3Br_4, PCl_3Br_8 and PCl_3Br_{18} in the fused state [1] that their conductivity increases with increasing Br content; with rising temperature the conductivity at first rises and then falls.

Since these conductive complexes are thermally unstable, it may be suggested that their thermal dissociation:

$$PCl_3(Br_2)_{n+1} \rightleftarrows PCl_3(Br_2)_{n-1} + Br_2 \cdots \rightleftarrows PCl_3 + nBr_2,$$

leading ultimately to nonconductive substances (PCl_3 and Br_2), decreases with increasing bromine content.

For the purpose of further examination of this phenomenon, we decided to study the electric conductivity of PCl_3Br_4, PCl_3Br_8 and PCl_3Br_{18} in an organic solvent (nitrobenzene)

TABLE 2

PCl_3Br_4 – Nitrobenzene System

PCl_3Br_4 (mole %)	Specific electric conductivity
1.36	$1.07 \cdot 10^{-4}$
3.75	$2.48 \cdot 10^{-3}$
5.35	$2.90 \cdot 10^{-3}$
6.41	$5.47 \cdot 10^{-3}$
7.63	$6.49 \cdot 10^{-3}$
13.49	$1.05 \cdot 10^{-2}$
14.53	$1.15 \cdot 10^{-2}$
24.60	$1.49 \cdot 10^{-2}$
36.53	$1.81 \cdot 10^{-2}$
41.21	$2.11 \cdot 10^{-2}$
48.77	$2.43 \cdot 10^{-2}$
49.01	$2.54 \cdot 10^{-2}$
55.60	$2.86 \cdot 10^{-2}$
61.60	Part of sample did not dissolve

TABLE 3

PCl_3Br_8 – Nitrobenzene System

PCl_3Br_8 (mole %)	Specific electric conductivity
2.76	$1.41 \cdot 10^{-3}$
6.05	$4.80 \cdot 10^{-3}$
16.02	$1.35 \cdot 10^{-2}$
23.43	$1.89 \cdot 10^{-2}$
33.68	$2.49 \cdot 10^{-2}$
40.56	$2.67 \cdot 10^{-2}$
50.41	$3.23 \cdot 10^{-2}$
55.06	$3.41 \cdot 10^{-2}$
83.11	$4.03 \cdot 10^{-2}$
100.0	$4.23 \cdot 10^{-2}$

TABLE 4

PCl_3Br_{10} – Nitrobenzene System

PCl_3Br_{10} (mole %)	Specific electric conductivity
6.46	$1.02 \cdot 10^{-2}$
10.76	$1.67 \cdot 10^{-2}$
16.25	$2.41 \cdot 10^{-2}$
30.79	$3.87 \cdot 10^{-2}$
39.77	$4.56 \cdot 10^{-2}$
50.12	$5.08 \cdot 10^{-2}$
56.24	$4.32 \cdot 10^{-2}$

Nitrobenzene was selected because it is a good solvent for the complexes in question and forms conductive solutions; also it is adequately stable in presence of the phosphorus chlorobromides (it is not brominated by them under the experimental conditions). The PCl_3Br_4 and PCl_3Br_{10} were prepared as described in the previous paper [1]; the PCl_3Br_8 was prepared by mixing PCl_3 and bromine in stoichiometrical proportions.

The specific electric conductivity of all of the solutions was measured at $20 \pm 0.1°$. Results appear in Tables 2-4 and in Figure 2.

The electric conductivity of solutions of PCl_3Br_4 and PCl_3Br_8 rises rapidly with increasing concentration (this is particularly conspicuous in PCl_3Br_{10} solutions), and then slows down until values of the order of 10^{-2} ohm^{-1}cm^{-1} are obtained. The electric conductivity of PCl_3Br_{10} solutions also increases with the concentration but relatively slows, and in the concentration region of more than 53 mole % it even falls off slightly. A comparison of the data of Tables 2-4 and of the isotherms shows that in general the electric conductivity of the investigated solutions increases in the order $PCl_3Br_4 < PCl_3Br_8 < PCl_3Br_{10}$, in analogy with the behavior of these substances in the fused state.

Measurements were also made of the electric conductivity (at some concentrations) of PCl_3Br_4 in acetonitrile in order to establish the order of magnitude of the conductivity. Such solutions are considerably better conductors than the nitrobenzene solutions especially in the region of low concentrations.

PCl_3Br_4 (mole %)	Specific electric conductivity
2.48	$9.28 \cdot 10^{-3}$
5.52	$2.08 \cdot 10^{-2}$
10.23	$3.38 \cdot 10^{-2}$

Benzene solutions of PCl_3Br_4, PCl_3Br_8 and PCl_3Br_{10} do not conduct electricity, nor do the solutions in CCl_4 and CS_2.

On dissolving these complexes in toluene and acetone a violent bromination reaction takes place, accompanied by evolution of gases.

Measurement of the Electric Conductivity of the System PCl_5–Br_2 in Nitrobenzene

These measurements were performed for the purpose of supplementing the foregoing investigations of nitrobenzene solutions of PCl_3Br_4

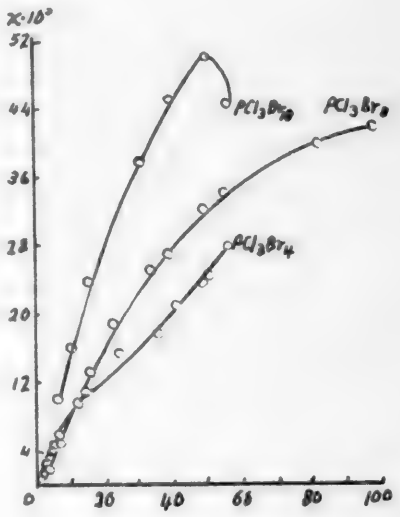

Figure 2. Specific electric conductivity of nitrobenzene solutions of PCl_3Br_4, PCl_3Br_8, and PCl_3Br_{10}.

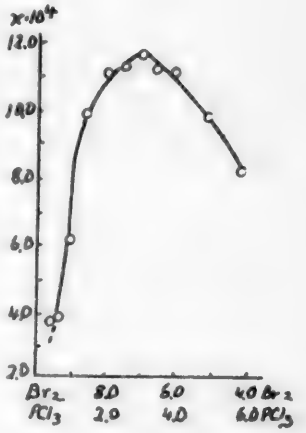

Fig. 3. Specific electric conductivity of the system PCl_5–Br_2 in nitrobenzene

and other complexes and with the special aim of establishing which of these chlorobromides predominates in nitrobenzene solutions of the system PCl_3-Br_2 containing various ratios of the components.

In order to ensure that these measurements should give results approximating to those of physico-chemical analysis we used the method of Ostromyslensky [4], Job [5], i.e., we prepared equimolecular solutions of PCl_3 and bromine in nitrobenzene and for each experiment we took that number of milliliters of these solutions which resulted only in a change in the ratio of PCl_3 to Br_2 while the total number of moles remained constant. Since the solutions of PCl_3 and bromine in nitrobenzene (taken separately) do not conduct electricity, we could utilize direct experimental data for graphical representation of the results of measurements (i.e., without determining deviations from additivity).

The results of these measurements are presented in Table 5 and Figure 3.

TABLE 5

Electric Conductivity of the System PCl_3-Br_2 in Nitrobenzene

Ratio of volumes (ml) of solutions of Br_2 and PCl_3	Specific electric conductivity at 20°
9.5:0.5	$3.66\cdot10^{-6}$
9.3:0.7	$3.77\cdot10^{-6}$
9.0:1.0	$6.13\cdot10^{-6}$
8.5:1.5	$9.85\cdot10^{-6}$
8.0:2.0	$1.12\cdot10^{-5}$
7.5:2.5	$1.13\cdot10^{-5}$
7.0:3.0	$1.17\cdot10^{-5}$
6.5:3.5	$1.13\cdot10^{-5}$
6.0:4.0	$1.11\cdot10^{-5}$
5.0:5.0	$1.11\cdot10^{-5}$
4.0:6.0	$8.11\cdot10^{-6}$

The results of these experiments strengthen the supposition that phosphorus trichloride combines with bromine in nitrobenzene solutions to form phosphorus chlorobromides. The maximum on the electroconductivity isotherm corresponds to a region of concentrations very close to the composition of the complex PCl_3Br_4.

We may conclude from these data that when the phosphorus chlorobromides dissolve in nitrobenzene they dissociate with cleavage of part of the bromine and an equilibrium, as represented in the schema on p. 1336 is established.

Electrolysis of Nitrobenzene Solutions of PCl_3Br_4 and PCl_3Br_{12}

An experimental study was made of the ionic transfer in nitrobenzene solutions of PCl_3Br_4 and PCl_3Br_{12} in order to investigate the nature of the ions into which these complexes dissociate.

The form of the vessels used, the working procedure and the analytical methods were described in a previous paper [6].

The duration of electrolysis was 1) 4 hours and 2) $6\frac{1}{2}$ hours; the current strength was 1) 4.5 A and 2) 15 A. During electrolysis the color of the anodic liquid gradually darkened, but the cathodic liquid became considerably lighter in color.

The results of these experiments are shown in Tables 6 and 7.

TABLE 6

Electrolysis of the $PCl_3Br_4-C_6H_5NO_2$ System

PCl_3Br_4 (Wt.%)	Element determined	Catholyte			Anolyte		
		Theoretical (g)	Found after electrolysis (g)	Difference (g)	Theoretical (g)	Found after electrolysis (g)	Difference (g)
9.66	Br	0.5956	0.4828	−0.1128	0.6911	0.8018	+0.1108
	Cl	0.1981	0.2708	+0.0727	0.2298	0.1543	−0.0755
	P	0.0578	0.0756	+0.0178	0.0631	0.0452	−0.0179

TABLE 7

Electrolysis of the PCl_3Br_{12} – Nitrobenzene System

PCl_3Br_{12} (Wt.%)	Element determined	Catholyte			Anolyte		
		Theoretical (g)	Found after electrolysis (g)	Difference (g)	Theoretical (g)	Found after electrolysis (g)	Difference (g)
15.28	Br	1.0424	0.8136	−0.2288	1.3099	1.5304	+0.2205
	Cl	0.0962	0.1539	+0.0577	0.1201	0.0599	−0.0602
	P	0.0314	0.0545	+0.0231	0.0393	0.0164	−0.0228

On calculating the ratios in which phosphorus and chlorine migrate to the anolyte, we find that each atom of phosphorus corresponds to the following numbers of gram-atoms of chlorine: 3.6 (in experiments with PCl_3Br_4) and 2.3 (in experiments with PCl_3Br_{12}). The corresponding figures for bromine are: 2.5 (with PCl_3Br_4) and 4.8 (with PCl_3Br_{12}).

The smaller amount of bromine transferred to the anolyte is evidently due to partial decomposition of the complexes in nitrobenzene

solution, this process being accompanied by cleavage of part of the bromine content, in consequence of which the investigated solutions actually contain complexes whose bromine content is lower than would correspond to their composition in the solid state. Furthermore, if we start from the general formula which we suggested for these complexes, $[PCl_3Br][Br(Br_2)_n]$, then part of the bromine must migrate to the cathode in the form of a complex cation, and this would also slightly reduce the quantity of bromine in the anodic portion of the solution.

EVALUATION OF THE RESULTS

Comparing the results of investigation of the system PCl_3-Br_2 with the experimental data presented in the first communication [1], we must first direct attention to the disagreement between the results of thermal analysis and of determination of the viscosity of the system.

The fusion diagram of the system PCl_3-Br_2 revealed the formation of two complexes – PCl_3Br_4 and PCl_3Br_{18}. These investigations failed to reveal the existence of PCl_3Br_8 which has been mentioned in the literature [7]. In the concentration region (20 mole % PCl_3) corresponding to this complex we found on the fusion diagram a eutectic with m.p. 15.1-15.5°. On the other hand the change in viscosity points to the existence of the complex PCl_3Br_8 in the liquid phase. The flat maximum is evidence of the instability of this complex.

A similar type of phenomenon has been noted in the literature, mainly in the papers of N.S.Kurnakov and his co-workers. For example, Kurnakov, Krotkov and Oksman [8] investigated the system $SbBr_3-(C_6H_5)3CH$ and found on the viscosity isotherms a maximum which did not change with the temperature, and on the fusion diagram only one eutectic, the viscosity maximum corresponding to the concentration region close to the eutectic composition.

Analogous observations were made by A.Vinogradova and N.Efremov [9], and by A.Tikhomirova and N. Efremov [10], in examining the systems phenol – methyl (or dimethyl) aniline and phenol – ethyl (or diethyl) aniline.

The absence of a maximum on the fusion diagram can be accounted for by the unfavorable conditions of crystallization of PCl_3Br_8 in the viscous medium.

Our experiments actually showed that the viscosity of the system PCl_3-Br_2 at a content of 20 mole % PCl_3 (at 25°) is nearly ten times higher than the viscosity of bromine. The viscosity isotherms of the system PCl_3-Br_2 are further characterized by the following features: a) The temperature coefficient of the viscosity is low at first but increases with the PCl_3 concentration and reaches a high value in the concentration region coinciding with the viscosity maximum, which provides further confirmation of the existence of the complex PCl_3Br_8 in the liquid phase. b) A minimum is observed on the viscosity isotherms in the region of 27-28 mole % PCl_3, following which the viscosity increases continuously up to the point of stratification of the system at a content of 33 mole % PCl_3, which corresponds to the complex PCl_3Br_4, and then the viscosity of the lower layer (fused PCl_3Br_4) becomes constant. Consequently the viscosity isotherms reflect the existence of this complex in addition to that of PCl_3Br_8.

The fact that the viscosity isotherm does not reflect the existence of PCl_3Br_{18} can be ascribed to partial dissociation of the complex in the liquid phase or to the general phenomenon that in the case of some complexes existing in the liquid phase, only those that are more stable under the experimental conditions are usually reflected on the viscosity diagram.

The measurement of the viscosity of PCl_3-Br_2 has thus supplemented our earlier results by showing that the existence of still another complex is possible in the liquid phase. The formation of the phosphorus chlorobromides of the general formula $PCl_3\cdot(Br_2)_n$, discussed in this paper, may be considered to proceed in the following manner: during the action of bromine on PCl_3, oxidation of the latter first takes place to the accompaniment of addition to it of one mole of bromine and the formation of the simplest chlorobromide of this type – PCl_3Br_2. *

When PCl_3Br_2 reacts with excess of bromine the former behaves like a halide of pentavalent phosphorus. As we know, PCl_5 and PBr_5 are capable of adding on bromine, when the complexes $PCl_5\cdot 5Br_2$ [11] and $PBr_5\cdot(Br_2)_n$ are formed, n being equal to 1.2 and 6 [12].

It may be assumed that the pentavalent phosphorus in this reaction, just as during interaction with iodine halides [6], is polarized according to the scheme $PX_5 \rightarrow [PX_4]X$; the anion X in the outer shell coordinates the molecules of halogens, iodine and chloride, iodine bromide, etc., which simultaneously strengthens the structure of the complex with the halogen-substituted phosphonium cation.

* As stated in the literature [13], this compound is extremely unstable and only exists at low temperatures. It decomposes when heated. Its instability is associated with stratification of the system PCl_3–bromine when the PCl_3 content exceeds 33 mole %.

On the basis of the preceding hypothesis, the following scheme may be advanced for the reaction of PCl_5 with bromine, it being assumed that the excess of bromine adds on to the bromine anion of the outer shell:

$$PCl_5 \xrightarrow{+Br_2} PCl_5Br_2 \longrightarrow [PCl_5Br]Br \xrightarrow{+Br_2} [PCl_5Br][Br(Br_2)_n].$$

The magnitude of n may vary from 1 to 8.

Consequently the simplest of these polybromides is $[PCl_5Br][Br(Br_2)]$ or PCl_5Br_4, while the most complex is $[PCl_5Br][Br(Br_2)_8]$ or PCl_5Br_{18}.

The results of experiments on the migration of ions in nitrobenzene solutions of the system PCl_5–Br_2 generally confirm the above structure of these phosphorus chlorobromides. The relative thermal instability of these complexes is consistent with the assumption that various intermediate forms between PCl_5Br_4 and PCl_5Br_{18} can exist in the fused state or in solution. It is to be hoped that these diverse complexes (with various magnitudes of n) will also be isolated in the crystalline form.

Although these phosphorus chlorobromides are relatively unstable, they do not undergo complete decomposition into the original PCl_5 and Br_2 when fused. The fused complexes have a high electric conductivity which first rises with the temperature and then (starting from 45-50°) falls off. On the other hand, PCl_5 and bromine in the free state do not conduct electricity at all.

The fact that the electric conductivity of the phosphorus chlorobromides increases in the order of PCl_5Br_4–PCl_5Br_8–PCl_5Br_{18}, i.e. with increasing bromine content, may be explained by the shifting to the left of the equilibrium of dissociation of these complexes:

$$PCl_5(Br_2)_n \rightleftarrows PCl_5(Br_2)_{n-1} + Br_2 \ldots \rightleftarrows PCl_5 + nBr_2.$$

SUMMARY

1. The viscosity of the system PCl_5–Br_2 was measured at 25 and 40° when a maximum was found at 20 mole % PCl_5, corresponding to a complex of the composition PCl_5Br_8. Two other complexes – PCl_5Br_4 and PCl_5Br_{18} – are indicated on the fusion diagram of this system.

2. The electric conductivity of these complexes in nitrobenzene solution increases with the concentration, attaining values of the order of 10^{-2} $ohm^{-1}cm^{-1}$, and also increasing in the order $PCl_5Br_4 < PCl_5Br_8 < PCl_5Br_{18}$.

3. Measurement of the electric conductivity of the system PCl_5–Br_2 in nitrobenzene by the method of isomolar concentrations (method of Ostromyslensky and Job) revealed the formation of products of addition of bromine to PCl_5, with PCl_5Br_4 as the most probable composition.

4. By means of the method of ionic migration it was shown that the structure of these phosphorus chlorobromides can be expressed by the following general formulas: $[PCl_5Br][Br(Br_2)_n]$. On the basis of thermal analysis of the system PCl_5–Br_2 and of investigations of the synthesis of chlorobromides, we may assume that n ranges between 1 and 8, which corresponds to the series of complexes starting from PCl_5Br_4 and finishing at PCl_5Br_{18}.

In their chemical nature these complexes may be regarded as polyhalides of tetracidophosphonium cations.

LITERATURE CITED

[1] Ya. A. Fialkov and A. A. Kuzmenko, J. Gen. Chem. 21, 433 (1951).*

[2] Ya. A. Fialkov and L. D. Muzyka, J. Gen. Chem., 20, 385 (1950).**

[3] Landolt, Bornstein, Tab. B. I (1923).

[4] L. Ostromyslensky, Ber. 44, 268 (1911).

[5] Job, Ann. Chim., 9, 113 (1928).

[6] A. A. Kuzmenko and Ya. A. Fialkov, J. Gen. Chem. 19, 1007 (1949).***

*See Consultants Bureau translation, p. 479.

**See Consultants Bureau translation, p. 407.

*** See Consultants Bureau translation, p. 997.

[7] Mellor. A comprehensive treatise on inorganic – theoret. Chemistry, VIII, 1042-1045 (1931).

[8] N. Kurnakov, D. Krotkov and M. Oksman, J. Russ. Phys. Chem. Soc., 47, 558 (1915).

[9] A. D. Vinogradova and N. N. Efremov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 143 (1937).

[10] A. M. Tikhomirova and N. N. Efremov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 157 (1937).

[11] V. A. Plotnikov and S. I. Yakubson, J. Russ. Phys. Chem. Soc. 60, 1513 (1928).

[12] Biltz and Jeep, Z. allg. anorg. Chem. 162, 32 (1927).

[13] Abegg's Handbuch d. anorg. Chem. B. 3, p. 417 (1907).

Received December 11, 1950

OXIDATION POTENTIALS OF HYPOCHLORITE SOLUTIONS

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The oxidizing ability and the character of the oxidizing action of hypochlorites depend in large measure upon the activity of the hydrogen ions in their solutions.

The dependence of the oxidizing properties on the pH is undoubtedly associated with the nature of hypochlorite solutions and certain features of the equilibria which are established in these solutions.

In 1900 were published the classic studies of Professor A. A. Yakovkin on the equilibrium of chlorine hydrolysis [1]:

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HClO. \qquad (1)$$

The hydrolysis constants which he obtained enable exact relations to be found between the chlorinating and the true oxidizing action of hypochlorites. A good deal of work has been devoted to the determination of the dissociation constant of hypochlorous acid, and values usually within the range of 10^{-8}–10^{-7}, have been reported. The equilibria of the two processes – hydrolysis of chlorine and dissociation of hypochlorous acid – govern the state of a solution of hypochlorous acid at different pH values.

Calculations show that alkaline solutions (pH > 10) contain substantially only ClO^- ions. Solutions whose pH is in the range 8.5-6.0 contain hypochlorous acid and its salt in approximately equal amounts. Solutions whose pH is below 5 are substantially free from salt.

Strongly acid solutions (pH < 3) contain, in addition to hypochlorous acid, appreciable amounts of chlorine ions. The ratio of the two components in such solutions at various pH values is governed by the hydrolysis constant of chlorine.

Hypochlorite solutions are not equilibrium systems by virtue of the fact that slow processes of decomposition accompanied by formation of chlorates or oxygen proceed arbitrarily in them.

The stability of these solutions is determined by the pH. Thus it has been found that the mechanism of conversion of hypochlorite into chlorate varies according to whether the reaction proceeds in alkaline, neutral or acidic media. The velocity of the process likewise varies. The latter was found [2] to be a minimum in a strongly acidic medium (pH $\cong$ 1); with increasing pH it rises and attains a maximum in a nearly neutral medium (pH $\cong$ 6.7); the conversion velocity begins to fall again in an alkaline medium.

We see that the activity of H^+ ions is one of the fundamental factors governing not only the oxidizing properties of hypochlorite solutions but also their composition and stability. An accurate characterization of this influence would clearly permit a deeper insight into the properties and nature of hypochlorite solutions. More precise knowledge of the effect of pH on the oxidizing properties may be obtained by an investigation of the oxidation potentials of these solutions.

Very few papers have been published on the dependence of oxidation potentials on pH in hypochlorite solutions, and these publications are lacking in full details of either the oxidation potentials themselves or of the equilibria governing them. We were therefore prompted to carry out an investigation of the dependence of the oxidation potentials of hypochlorite solutions on the pH.

EXPERIMENTAL

In alkaline solutions of hypochlorite the oxidation potential may be governed by electrode reaction:

$$ClO^- + 2H^+ + 2e \rightleftharpoons Cl^- + H_2O. \qquad (2)$$

In neutral and, especially, in weakly acidic solutions in which ClO^- ions change into HClO, we may expect the following reaction instead of (2):

$$HClO + H^+ + 2e \rightleftharpoons Cl^- + H_2O. \quad (3)$$

Finally, in very acidic solutions in which chlorine is liberated according to reaction (1), the oxidation potential is determined by the electrode process:

$$Cl_2 + 2e = 2Cl^-. \quad (4)$$

It follows from equations (2) and (3) that the oxidation potential must depend on the pH (since it differs in the acidic and alkaline regions) and also on the concentrations of hypochlorite and chlorine ions. In the strongly acid region, where the equilibrium of reaction (1) is sharply shifted to the left, we should expect the oxidation potential to be independent of the pH according to equation (4). The experimental investigation of these relationships will also be dealt with in this paper.

In the first instance measurements were made of the oxidation potentials in freshly prepared solutions of sodium hypochlorite and bleaching powder.

Sodium hypochlorite was prepared by passing chlorine into a solution of sodium hydroxide. The calcium hypochlorite solutions were perfectly transparent and colorless. They were stored in the dark in a dark-glass container. The oxidation potentials were measured with the help of a platinum gauze electrode. The pH of the solutions was determined with an electrode of ES-1 glass (72% SiO_2; 6% CaO; 22% Na_2O). The pH and the oxidation potentials were measured on a lamp potentiometer. The measurements with the glass electrode were accurate to within about 1 mV. A platinum electrode and a potassium chloride-agar siphon, for connection to the calomel electrode, were inserted simultaneously in a beaker closed with a waxed rubber stopper. Through another hole in the stopper was passed the tip of a small buret from which acid or alkali was run into the solution. The second half-element for the measurements was a saturated calomel electrode. All the values of oxidation potentials presented below are expressed in relation to this electrode.

In order to reduce the values of φ to the hydrogen zero point, they must be increased by the value of the potential of the saturated calomel electrode at 18°, i.e. by +0.250 V.

The starting solutions placed in the beaker were either chlorine water or a solution of sodium hypochlorite containing an excess of alkali or a solution of bleaching powder containing an excess of $Ca(OH)_2$. Since hypochlorite solutions only develop a buffering action in the pH range of 8-6, a more detailed study of the effect of pH upon the oxidation potential necessitated buffering of the solutions with boric, acetic or monochloracetic acid.

In the alkaline region the oxidation potential was established slowly at the platinum electrode. A special investigation showed that a constant potential in a solution with pH $\cong$ 10.5 is only reached after several hours. Consequently measurements carried out in this region were sometimes prolonged for 24 hours or longer. In this case the measurements were considered to be completed when the potential remained constant over a period of several hours. In the neutral and acid regions a steady potential was established more quickly, so that the duration of the pH measurements was then from 30 minutes to a few hours.

In Figures 1 and 2 are plotted the results of the potentiometric titrations. The upper curves characterize the pH change and the lower ones the change in oxidation potentials. Upper and lower curves are quite similar.

The individual portions of these curves correspond to the processes:

$$H^+ + OH^- \rightleftharpoons H_2O, \quad (5)$$
$$ClO^- + H^+ \rightleftharpoons HClO, \quad (6)$$
$$HClO + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O. \quad (1)$$

The positions of the inflection points of the upper and lower curves coincide on the axis of the abscissas. These inflection points separate from each other the above-noted portions of the titration curves. The identical course of the pH and oxidation potential curves is particularly marked in Figure 3 in which both curves are plotted with an identical scale along the axis of the ordinates (one pH unit corresponds to 58mV of oxidation potential); here the pH values on the ordinates increase from bottom to top, while the values of φ increase from top to bottom.

Analysis showed the content of hypochlorite determined from the titration curve (from the length of the corresponding portion along the axis of the abscissas), agrees with measurements by the iodometric method. The potentiometric titration curves consequently offer the possibility of exact determination of the content of free alkali and active chlorine in a hypochlorite solution, as will be discussed more fully in another paper.

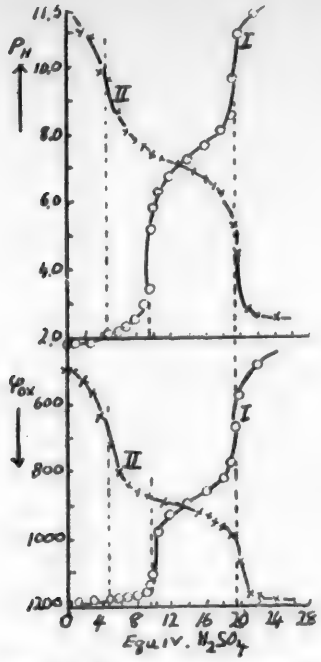

Figure 1. I) Titration of chlorine water with sodium hydroxide; II) titration of sodium hypochlorite with sulfuric acid.

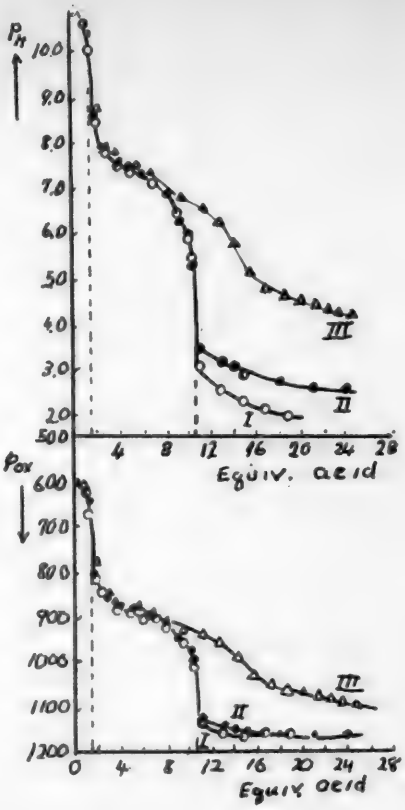

Figure 2. I) Titration with HCl solution; II) titration with monochloracetic acid solution; III) titration with acetic acid solution.

From Figures 1 and 2 and, in particular from Figure 3, it is clear that a definite dependence does actually exist between the oxidation potential and the pH in hypochlorite solutions. This dependence is illustrated in Figure 4. Here are plotted the results of our measurements in hypochlorite solutions (0.0289 N) prepared from chlorine water, and in bleaching powder solutions (0.0293 N). There is substantial agreement between the results of both sets of measurements.

It is interesting to compare the results obtained with the data of other authors. Remington and Trimble [3] give the oxidation potentials measured by them in hypochlorite solutions with the help of a platinum foil electrode. Their solutions were buffered in the pH range of 5.29-8.04 with a phosphate mixture and in the pH range of 8.35-11.59 with a carbonate mixture. Apparently the pH of the solutions was not accurately measured in these experiments.

In this paper it was established that a break in the straight-line dependence occurs in the pH region around 9-8, which the authors attribute to a "solvation" effect associated in their opinion with the use of different buffer systems.

Hisey and Koon [4], who performed measurements in calcium chlorate solutions, show that the rectilinear dependence begins to break down at pH < 5.0. Høye [5] made more systematic and accurate measurements of potentials in hypochlorites prepared from chlorine water and presented data which indicate the start of deviation from linearity in a more acidic region (much lower than pH = 5.0).

Our own data reveal the presence of an inflection on the curve in the pH range of approximately 9.3-8.8. Below pH = 8.8 and above pH = 9.3 a rectilinear dependence of the oxidation potential on the pH is observed with the same slope.

This procedure of course results in a deviation from experimental values at pH > 9.0. With further acidification the calculated values of the oxidation potential (at $\varphi_0 = 1.322$) begin to deviate from the experimental results (broken curve II on Fig. 5). Comparison of formulas (7) and (8) shows that with increasing HClO content of the solution the angle of slope of the straight line $\varphi = \varphi(pH)$ is bound to decrease (from 58 to 29 mV per pH unit).

However, experiments have failed to reveal such a change in the slope of the straight line, associated with the transformation of ClO^- into HClO, down to pH $\cong$ 3.5, at which point the change is evidently due to another cause. This permits us to draw the conclusion that the formation of HClO does not influence the oxidation potential. This conclusion is not in accord with the widely held opinion that the oxidizing ability of HClO is greater than that of its salt. Therefore from the absence of an effect of Cl^- upon the oxidation potential and from the presence of an inflection on the $\varphi = \varphi(pH)$ rectilinear plot in the region of approximately 9.3-8.9, it follows that the oxidation potential in the pH range of 9.0-3.5 is not governed by the equilibria on which formulas (7) and (8) are based.

Since the ClO_3^- ions have no effect upon the oxidation potential, it may be inferred that the processes of decomposition of hypochlorites with formation of chlorates, for example:

$$ClO_3^- + 2H^+ + 2Cl^- \rightleftharpoons 2HClO + ClO^-, \qquad (9)$$

likewise do not govern the potentials. The experimental data can likewise not be explained by the fact that the electrode behaves like an oxygen electrode due to the processes:

$$ClO^- \rightleftharpoons Cl^- + \frac{1}{2} O_2. \qquad (10)$$

or

$$HClO \rightleftharpoons H^+ + Cl^- + \frac{1}{2} O. \qquad (11)$$

In this case the electrode potentials ought to be considerably lower than the experimental values (Fig. 5).

An understanding of the equilibria which govern the potential in this pH region calls for further investigation of the properties of hypochlorite solutions.

In the more acidic region (pH < 3.5) chlorine begins to be formed in appreciable amounts in the solution. On this basis we may suggest that the deviations from rectilinearity of the curve (Fig. 5) in the strongly acidic region (pH > 3.0) are due to the influence of the equilibrium of chlorine hydrolysis on the oxidation potential.

Here the oxidation potential of the solution must be determined by the system Cl_2–Cl^-, i.e. the electrode begins to behave like a chlorine electrode.

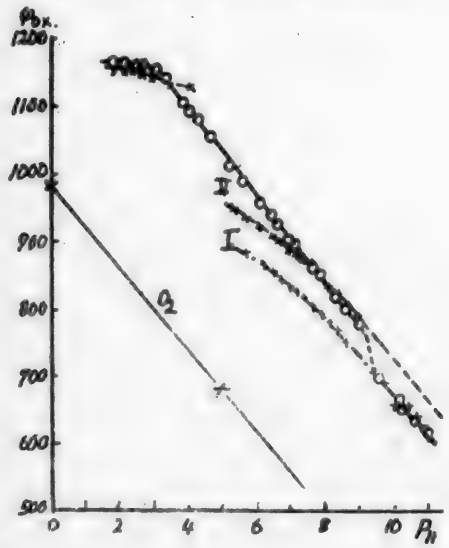

Figure 5. Circles relate to experimental values; crosses to calculated values.

If these considerations are valid, then its potential is:

$$\varphi_{Cl_2/Cl^-} = \varphi^0_{Cl_2/Cl^-} + \frac{2}{2} \log \frac{a_{Cl_2}}{a^2_{Cl^-}}. \qquad (12)$$

Applying the law of mass action to the hydrolysis of chlorine (1), we get:

$$a_{Cl_2} = k'_h \, a_{H^+} \cdot a_{Cl^-} \cdot a_{HClO}, \text{ where } k'_h = \frac{1}{k_h}; \quad (a)$$

where k_h is the hydrolysis constant of chlorine. According to Yakovkin, at 18°, $k_h = 3.75 \cdot 10^{-4}$.

We denote the initial concentrations of hypochlorous acid and chlorides by respectively:

$$a^0_{HClO} = a_{HClO} + a_{Cl_2}, \qquad (b)$$

$$a^0_{Cl^-} = a_{Cl^-} + a_{Cl_2}. \qquad (c)$$

From expressions (a), (b) and (c) we find:

$$a_{Cl_2} = k'_h \, a_{H^+} \cdot a_{Cl^-} \cdot (a^0_{HClO} - a^0_{Cl^-} + a_{Cl^-}). \qquad (d)$$

The value of a_{Cl^-} can be obtained by simultaneously solving equations (c) and (d). $\varphi_0 Cl_2/Cl^- = 1.359$ V (in relation to the normal hydrogen electrode).

Since $\varphi_0 Cl_2/Cl^-$ is given for the equilibrium pressure of chlorine equal to one atmosphere, the oxidation potential towards the saturated calomel electrode is:

$$\varphi_{Cl_2/Cl^-} = 1.109 + \frac{\vartheta}{2} \log \frac{p_{Cl_2}}{a^2_{Cl^-}},$$

where p_{Cl_2} is the equilibrium pressure of chlorine at its concentration (activity) in solution equal to a_{Cl_2}.

According to Winkler the solubility of chlorine at a pressure of one atmosphere and a temperature of 20° is 0.7923 g per 100 g water, or 0.105 mole/l.

Taking $\frac{p_{Cl_2}}{a_{Cl_2}} = \frac{1}{0.105}$, we obtain:

$$\varphi_{Cl_2/Cl^-} = 1.109 - \frac{\vartheta}{2} \log 0.105 + \frac{\vartheta}{2} \log \frac{a_{Cl_2}}{a^2_{Cl^-}} V. \qquad (13)$$

The oxidation potentials for values of pH $<$ 4 calculated according to equation (12) are shown by crosses in Figure 5.

We see from Figure 5 that the calculated values are in adequate agreement with the experimental ones. This shows that the platinum electrode actually behaves like the chlorine electrode in the pH region below 3.5.

SUMMARY

1. In hypochlorite solutions with pH $>$ 9.3 the oxidation potential changes with changing concentration of ions of H^+, ClO^- and Cl^-. In this region the potential may be calculated from the formula:

$$\varphi = \varphi_0 - \vartheta pH + \frac{\vartheta}{2} \log \frac{a_{ClO^-}}{a_{Cl^-}}, \text{ where } \varphi_0 = 1.267 \text{ V}.$$

2. In solutions with a pH from 8.5 to 4.0 the dependence of the oxidation potential on the pH is represented by a straight line lying 55-60 mV higher than the straight line obtained in the alkaline region (pH greater than 9.3).

In this region the potential does not change with changing concentration of Cl^- ions in the solution. The oxidation potential in this region is not governed by the equilibria:

$$ClO^- + 2H^+ + 2e \rightleftharpoons Cl^- + H_2O \text{ and } HClO + H^+ + 2e \rightleftharpoons Cl^- + H_2O.$$

3. An influence of chlorate ions on the oxidation potential in alkaline, neutral and weakly acid regions could not be detected.

4. In solutions with a pH below 3.5 the electrode potential is governed by the equilibrium of chlorine hydrolysis. In this region the electrode behaves like a chlorine electrode.

LITERATURE CITED

[1] A. A. Yakovkin, J. Russ. Phys. Chem. Soc. 32, 673 (1900).

[2] R. W. Chapin, J.Chem.Soc., 56, 2211 (1934).

[3] V. H. Remington and H. M. Trimble, J. Phys. Chem. 33, 424 (1929).

[4] W. O. Hisey and C. M. Koon, Pap. Trade J. 36, 6 (1936).

[5] L. Høye, Kg. Norske Widenskol. Torn. 16, 8 (1943).

Received November 10, 1950.

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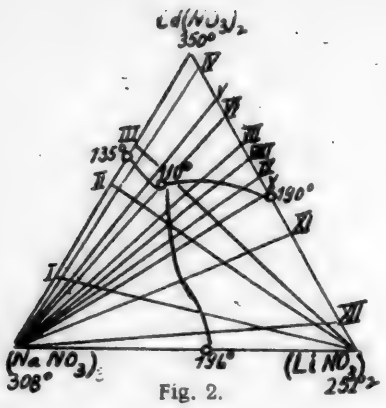

Fig. 2.

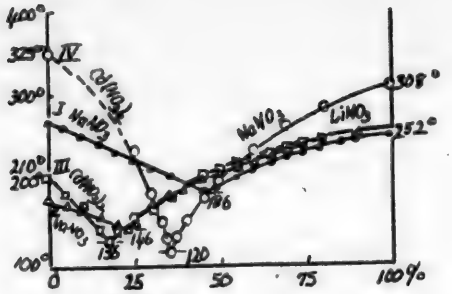

Fig. 3.

3. We have also been the first to investigate the binary system cadmium nitrate-sodium nitrate. The fusion curve of this system consists of two branches — a branch of the primary crystallization of cadmium nitrate descending very steeply to the eutectic point. The eutectic point corresponds to 36% sodium nitrate and 46% cadmium nitrate, with a melting point of 135° (Fig. 1).

The system was investigated in the range from 15% sodium nitrate. As in the previously described system, a lower content of sodium nitrate resulted in decomposition of the melts with evolution of nitrogen peroxide. Melts of salts containing 60-70% cadmium nitrate readily changed into the vitreous state which seriously retarded the development of crystals.

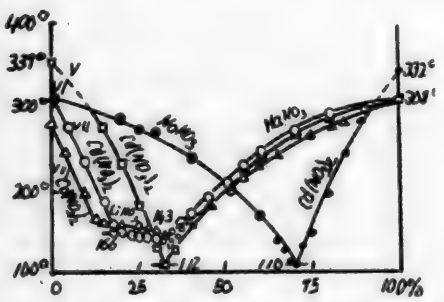

Fig. 4.

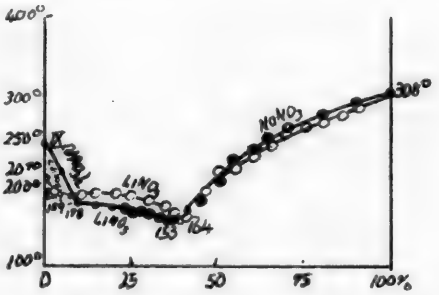

Fig. 5.

Ternary sections. For the purpose of investigation of the liquidus surface of the ternary system, in accordance with the general principles of physico-chemical analysis, 12 sections (Figure 2) were examined.

Section I: 25% $Cd(NO_3)_2$ + 75% $(NaNO_3)_2$ ⟶ $(LiNO_3)_2$. The phase diagram of the section comprises two branches: A branch of primary crystallization of sodium nitrate and a branch of primary crystallization of lithium nitrate (Fig. 3). The transition point corresponds to the composition: 46% lithium nitrate, 13.25% cadmium nitrate, 40.75% sodium nitrate, and a temperature of 168°.

Section II: 55% $Cd(NO_3)_2$ + 45% $(NaNO_3)_2$ ⟶ $(LiNO_3)_2$. The phase diagram of the section consists of two branches: A branch of sodium nitrate crystallization and a branch of lithium nitrate crystallization. The transition point corresponds to the composition: 23% lithium nitrate, 42.25% cadmium nitrate, 34.75% sodium nitrate, and a temperature of 146°.

Section III: 70% $Cd(NO_3)_2$ + 30% $(NaNO_3)_2$ ⟶ $(LiNO_3)_2$. The phase diagram of the section consists of two branches: A cadmium nitrate crystallization branch and a lithium nitrate crystallization branch. The transition point corresponds to the composition: 18% lithium nitrate, 57.5% cadmium nitrate, 24.5% sodium nitrate and a temperature of 136° (Fig. 3).

Section IV: 5% $(LiNO_3)_2$ + 95% $Cd(NO_3)_2$ ⟶ $(NaNO_3)_2$. The section was investigated from 25% sodium nitrate. At a lower content of sodium nitrate, the melt decomposes with evolution of nitrogen peroxide. The

liquidus curve of the section consists of two crystallization branches: A cadmium nitrate and a sodium nitrate branch. The transition point corresponds to the composition: 35.5% sodium nitrate, 3.2% lithium nitrate, 61.3% cadmium nitrate, and a temperature of 120° (Fig. 3). At certain quantitative ratios of the components the melts readily change into a glassy modification.

Section V: 15% $(LiNO_3)_2$ + 85% $Cd(NO_3)_2$ ⟶ $(NaNO_3)_2$. The section was studied from the point corresponding to 15% sodium nitrate. At a lower content of the latter (as in the preceding section) the melts decompose. The liquidus curve of the section consists of two branches, one being the crystallization curve of cadmium nitrate and the other the crystallization curve of sodium nitrate. The transition point is at the composition: 32.5% sodium nitrate, 10.25% lithium nitrate and 57.25% cadmium nitrate and a temperature of 112°. In melts containing from 27.5 to 32.5% sodium nitrate, vitrification is observed (Fig. 4).

Section VI: 20% $(LiNO_3)_2$ + 80% $Cd(NO_3)_2$ ⟶ $(NaNO_3)_2$. The phase diagram of the section consists of two branches: A cadmium nitrate crystallization branch and a sodium nitrate crystallization branch. The transition point corresponds to the composition: 29.5% sodium nitrate, 14.5% lithium nitrate, 56% cadmium nitrate and a temperature of 110°. Vitrification was observed in melts with a sodium nitrate content of 25 to 30% (Fig. 4).

Section VII: 30% $(LiNO_3)_2$ + 70% $Cd(NO_3)_2$ ⟶ $(NaNO_3)_2$. The section consists of three crystallization branches: Cadmium nitrate, lithium nitrate and sodium nitrate. The first transition point corresponds to the composition: 18% sodium nitrate, 25% lithium nitrate, 57% cadmium nitrate and a temperature of 156°. The second transition point corresponds to the composition: 32% sodium nitrate, 20.75% lithium nitrate, 47.25% cadmium nitrate and a temperature of 140° (Fig. 4). The salt melts on certain portions of the liquidus curve possess a high viscosity and readily change into the vitreous state.

Section VIII: 35% $(LiNO_3)_2$ + 65% $Cd(NO_3)_2$ ⟶ $(NaNO_3)_2$. The section possesses three crystallization branches: cadmium nitrate, lithium nitrate and sodium nitrate. The first transition point corresponds to the composition: 13.5% sodium nitrate, 30.5% lithium nitrate, 56% cadmium nitrate and a temperature of 166°. The second transition point corresponds to the composition: 34% sodium nitrate, 23.5% lithium nitrate, 42.5% cadmium nitrate and a temperature of 143°. Melts of the salts containing between 46 and 55% of cadmium nitrate are very viscous (Fig. 4).

Section IX: 40% $(LiNO_3)_2$ + 60% $(CdNO_3)_2$ ⟶ $(NaNO_3)_2$. The section consists of three crystallization branches: Cadmium nitrate, lithium nitrate and sodium nitrate. The first transition point corresponds to the composition: 9.25% sodium nitrate, 36.5% lithium nitrate, 54.25% cadmium nitrate and a temperature of 178°. The second transition point corresponds to the composition: 36% sodium nitrate, 26.75% lithium nitrate, 38.25% cadmium nitrate and a temperature of 153° (Fig. 5).

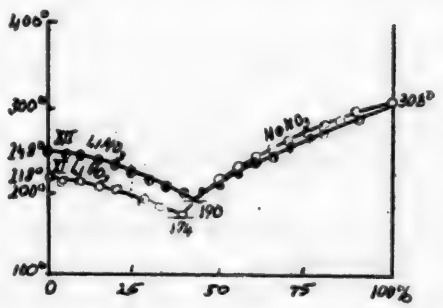

Fig. 6.

Section X: 45% $(LiNO_3)_2$ + 55% $(CdNO_3)_2$ ⟶ $(NaNO_3)_2$. The section has three crystallization branches: Cadmium nitrate, lithium nitrate and sodium nitrate. To the first transition point corresponds the composition: 2.5% sodium nitrate, 44% lithium nitrate, 53.5% cadmium nitrate and a temperature of 189°. To the second transition point corresponds the composition: 37.5% sodium nitrate, 28.25% lithium nitrate, 34.25% cadmium nitrate and a temperature of 164° (Figure 5).

Section XI: 60% $(LiNO_3)_2$ + 40% $Cd(NO_3)_2$ ⟶ $(NaNO_3)_2$. The section possesses two crystallization branches: Lithium nitrate and sodium nitrate. The transition point corresponds to the composition: 40%

sodium nitrate, 36% lithium nitrate, 24% cadmium nitrate and a temperature of 174° (Figure 6). Crystallization proceeded readily throughout the whole course of the section.

Section XII: 90% $(LiNO_3)_2$ + 10% $Cd(NO_3)_2$ ⟶ $(NaNO_3)_2$. The section has two crystallization branches: lithium nitrate and sodium nitrate. The transition point corresponds to the composition: 42.5% sodium nitrate, 52% lithium nitrate, 5.5% cadmium nitrate and a temperature of 190° (Fig. 6).

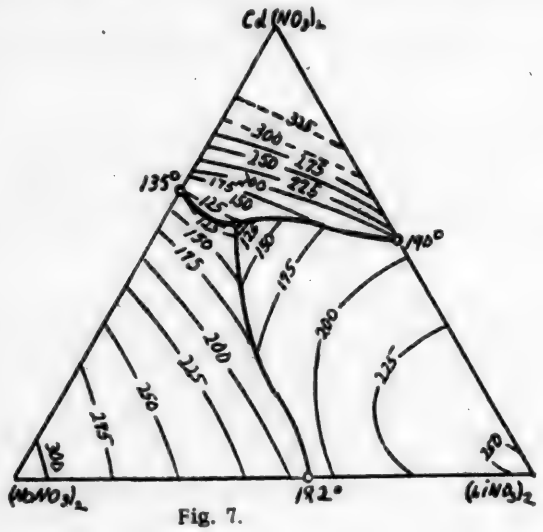

Fig. 7.

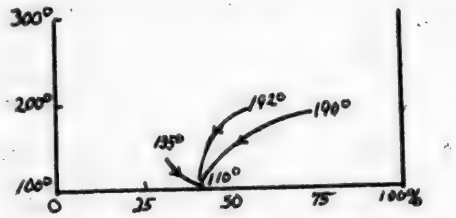

Fig. 8. Projection of the crystallization paths on the side of the sodium nitrate-lithium nitrate triangle

The experimental data for the ternary system are generalized in the projection of the triangular isothermal plots on the phase diagram. The isotherms are drawn through 25° (Fig. 7).

The investigated system of the nitrates of cadmium, sodium and lithium is a system with a simple eutectic, as was to be expected on the basis of the character of the binary systems.

Corresponding to the ternary eutectic point is the composition: 56% mole-% of cadmium nitrate, 14.5% mole-% of lithium nitrate, 29.5% mole-% of sodium nitrate and a melting point of 110° for the ternary eutectic.

The system is characterized by the presence of three crystallization fields:

a) A crystallization field of sodium nitrate comprising 39.12% of the total area of the triangle.

b) A field of crystallization of lithium nitrate with an area of crystallization of 42.5%.

c) A field of crystallization of cadmium nitrate extending over 18.38% of the total area of the triangle.

In Fig.8 is shown the orthogonal projection of the crystallization paths on the side of the sodium-nitrate-lithium nitrate triangle.

A study of this system revealed that the introduction of cadmium ions promoted vitrification. It must be pointed out that vitrification was observed in melts at certain concentrations of cadmium nitrate, which confirms the theory previously advanced by us [1].

Striking features of the ternary system of the nitrates of cadmium, sodium and lithium are the unusually low melting point of the ternary eutectic melt (110°) and the occurrence of vitrification.

SUMMARY

1. The ternary system of the nitrates of cadmium, sodium and lithium was investigated by the visual-polythermal method of physico-chemical analysis.

2. It was established that the system has one invariant point corresponding to the composition: 14.5% mole-% of lithium nitrate, 56% mole-% of cadmium nitrate, 29.5% mole-% of sodium nitrate and a melting point of 110°. It also possesses three fields of crystallization:

a) A cadmium nitrate field extending over 18.38% of the total area of the triangle.

b) A sodium nitrate field (39.12% of the area).

c) A lithium nitrate field (42.5% of the area).

3. It is shown that the largest field of crystallization, contrary to the established views, belongs to the least refractory component — lithium nitrate.

4. The field of formation of a low-melting glass from the nitrates is determined.

5. Two binary systems were studied:

a) Cadmium nitrate-sodium nitrate, which formed a system with the simple eutectic composition: 36% mole-percent of sodium nitrate and 64% mole-percent of cadmium nitrate, with a melting point of 135°.

b) Cadmium nitrate-lithium nitrate, likewise a system with a simple eutectic composition: 46.75% mole-percent of lithium nitrate and 53.25% mole-percent cadmium nitrate, with a melting point of 190°.

LITERATURE CITED

[1] P. I. Protsenko and A. G. Bergman, J. Gen. Chem. 20, 8, 1365 (1950). •

[2] P. I. Protsenko and A. G. Bergman, J. Gen. Chem. 21, 8, 1380 (1951). ••

[3] P. I. Protsenko and A. G. Bergman, J. Gen. Chem. 21, 9, 1587 (1951). •••

[4] P. I. Protsenko, Sci. Mem. of the Chemical Faculty of Rostov Univ. No. 5, 97-109 (1951).

[5] A. P. Palkin, S. D. Gromakov and others, Reactions in the absence of solvents, Voronezh, 7-14 (1939).

[6] deCesaris, Handbook of physical, chemical and technological values, Vol. 6, Moscow, 174 (1931).

[7] Carveth, Handbook of physical, chemical and technological values, Vol 6, Moscow, 184 (1931).

[8] V. P. Blidin, Bull. Sect. Phys. Chem. Anal., Inst. Inorg. Chem., 13, 191 (1940).

Received November 1, 1950

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• See Consultants Bureau translation, p. 1367.
•• See Consultants Bureau translation, p. 1509.
••• See Consultants Bureau translation, p. 1731.

REACTIONS OF NITRATES AND NITRITES OF METALS OF THE FIRST AND SECOND GROUPS OF THE PERIODIC SYSTEM IN MELTS

V. INVESTIGATION OF THE TERNARY SYSTEM OF THE NITRATES OF LITHIUM, POTASSIUM AND CADMIUM IN MELTS*

P. I. Protsenko

In a previous communication [1] it was shown that the nitrates of lithium, sodium and cadmium in melts, both in the binary and ternary systems, do not react chemically with one another but form low-melting eutectics. The substitution of sodium nitrate by potassium nitrate changes the character of the interaction of the components in the melts. Potassium nitrate with cadmium nitrate, as will be shown below, forms a congruent chemical compound – $Cd(NO_3)_2 \cdot 2KNO_3$, which is stable in melts and in the presence of a third component. Examination of this system revealed vitrification which was especially pronounced in the binary system of potassium and cadmium nitrates. The high degree of dispersity of the crystals in melts of the salts at certain concentrations of components and the increasing viscosity under such conditions greatly hindered the performance of the experiment.

Binary systems. 1. The system lithium nitrate–cadmium nitrate was first investigated by the author and has already been described [1].

2. The system lithium nitrate-potassium nitrate was studied by Carveth [2] according to whom the system is a simple eutectic. Corresponding to the eutectic point is the composition: 61.44% mole-% of potassium nitrate and 38.56% mole-% of lithium nitrate and a melting point of 139°. Our investigation confirmed the general character of the system but with slightly different data.

The eutectic point corresponds to the composition: 58% mole-% of potassium nitrate, 42% mole-% of lithium nitrate and a temperature of 120°** (Fig. 1).

As far as we are aware the binary system potassium nitrate-cadmium nitrate has not been described in the literature; we are the first to study it. The system has three crystallization branches; cadmium nitrate descending to the eutectic point (168°); the crystallization branch of the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$ with a maximum to which corresponds the temperature of 199.5°; and the crystallization branch of potassium nitrate. The cadmium nitrate branch could be followed from the ordinate of the composition corresponding to 20% potassium nitrate and 80% cadmium nitrate to the first eutectic point of 168°. Decomposition of the melt occurred on heating above 250°. The binary system of the nitrates of cadmium and potassium has two eutectics with a maximum. To the first eutectic point corresponds the composition: 37.5% potassium nitrate, 62.5% cadmium nitrate and a temperature of 168°.

To the second eutectic point corresponds the composition: 60% potassium nitrate and 40% cadmium nitrate and a temperature of 175°.

The maximum point, as already indicated above, corresponds to a temperature of 199.5° and the composition: 50% potassium nitrate and 50% cadmium nitrate (Fig. 1).

Investigation of this system involved considerable experimental difficulties since during the entire period of crystallization of cadmium nitrate occurred separation of highly dispersed crystals which led to a rise in viscosity and to vitrification.

Ternary sections. In order to elucidate the character of the interaction of the nitrates of cadmium, potassium and lithium in melts, an investigation of 11 sections was undertaken. From the side of the triangle

* N. M. Shevchenko collaborated in the investigation.

** Throughout the composition will be expressed as mole-equivalent percentages.

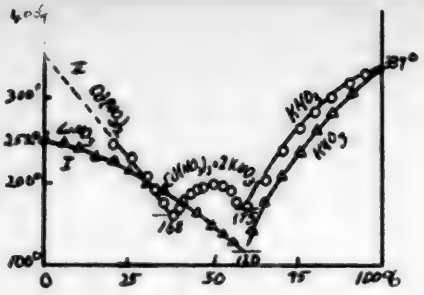

Fig. 1.

I) $LiNO_3 \rightarrow KNO_3$;
II) $Cd(NO_3)_2 \rightarrow (KNO_3)_2$.

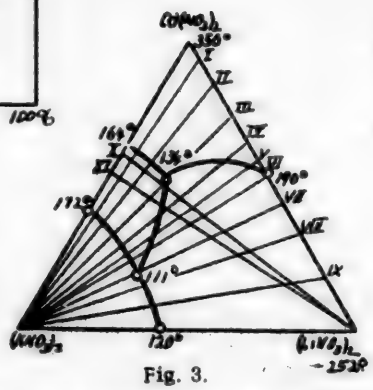

Fig. 3.

I) 95% $Cd(NO_3)_2$ + 5% $Li(NO_3)_2 \rightarrow (KNO_3)_2$;
II) 85% $Cd(NO_3)_2$ + 15% $Li(NO_3)_2 \rightarrow (KNO_3)_2$.

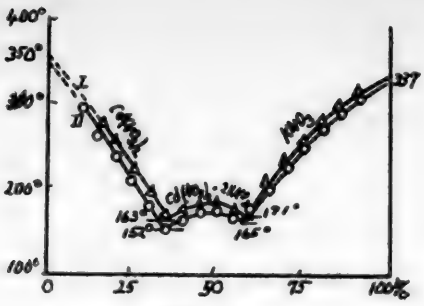

Fig. 2.

for cadmium nitrate—lithium nitrate to the apex of potassium nitrate were studied the sections I, II, III, IV, V, VI, VII, VIII and IX. From the side of the cadmium nitrate—potassium nitrate triangle to the lithium nitrate apex were studied sections X and XI (Figure 2).

Section I: 95% $Cd(NO_3)_2$ + 5% $(LiNO_3)_2 \rightarrow (KNO_3)_2$. This has three branches of crystallization: cadmium nitrate, descending to the transition point of 163°; the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$, and potassium nitrate. The temperatures and compositions at the transition points are: 1) 163° and 36.5% potassium nitrate, 3.5% lithium nitrate and 60% cadmium nitrate. 2) 171° and 58.75% potassium nitrate, 2.25% lithium nitrate and 39% cadmium nitrate. Corresponding to the maximum on the curve of the chemical compound is a temperature of 192° (Figure 3). The transition points found by intersection of the crystallization curves were also confirmed experimentally. Along the cadmium nitrate branch there was observed, at certain ratios of components, vitrification which seriously hindered crystallization.

Section II: 85% $Cd(NO_3)_2$ + 15% $(LiNO_3)_2 \rightarrow (KNO_3)_2$. This section has three crystallization branches: cadmium nitrate steeply descending to the transition point (152°); the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$; and potassium nitrate, likewise steeply rising from the transition point (165°).

This section possesses two transition points and a maximum. The first point is at 152° and has the composition: 34% potassium nitrate, 10% lithium nitrate and 56% cadmium nitrate; the second is at 165° and has the composition: 57.5% potassium nitrate, 6.5% lithium nitrate, and 36% cadmium nitrate.

The transition points were found by intersection of the crystallization curves. The maximum is at a temperature of 179° (Figure 3). Vitrification (which hindered crystallization) was observed on the potassium nitrate branch between the ordinates of the composition ranging from 15 to 34% potassium nitrate. Throughout the remaining extent of the liquidus curve, crystallization of the salts proceeded readily.

Section III: 75% $Cd(NO_3)_2$ + 25% $(LiNO_3)_2 \rightarrow (KNO_3)_2$. This has three crystallization branches: cadmium nitrate, descending in almost a straight line to 134°; the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$, enclosed between two transition points; and the potassium nitrate branch, steeply rising from 152°.

Section III has two transition points and a maximum point. Corresponding to the first transition point is a temperature of 134° and the composition: 32% potassium nitrate, 17% lithium nitrate, and 51% cadmium nitrate; to the second point corresponds the temperature of 152° and the composition: 56% potassium nitrate, 11% lithium nitrate, and 33% cadmium nitrate.

The temperature of 165° corresponds to the maximum (Figure 4).

Crystallization-hindering vitrification likewise takes place along the course of section III between the ordinates to which corresponds a composition with 10 to 30% potassium nitrate. Separation of the first crystals along the branch of crystallization of the chemical compound and of potassium nitrate was easily observed; the salt melts were transparent and crystallized well.

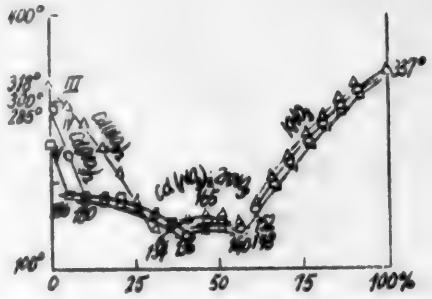

Fig. 4. III) 75% $Cd(NO_3)_2$ + 25% $(LiNO_3)_2$ → $(KNO_3)_2$; IV) 65% $Cd(NO_3)_2$ + 35% $(LiNO_3)_2$ → $(KNO_3)_2$; V) 60% $Cd(NO_3)_2$ + 40% $(LiNO_3)_2$ → $(KNO_3)_2$.

Section IV: 65% $Cd(NO_3)_2$ + 35% $(LiNO_3)_2$ → $(KNO_3)_2$. This is distinguished by four crystallization branches: cadmium nitrate, descending to 180°; lithium nitrate, also smoothly descending to 136°; the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$; and potassium nitrate. The first transition point corresponds to a temperature of 180° and the composition: 10% potassium nitrate, 31.5% lithium nitrate, and 58.5% cadmium nitrate. The second corresponds to 136° and the composition: 39% potassium nitrate, 22.2% lithium nitrate, and 38.8% cadmium nitrate. The third corresponds to 148° and the composition: 55% potassium nitrate, 16% lithium nitrate, and 29% cadmium nitrate.

The temperature of the maximum point is 158° (Figure 4).

Section V: 60% $Cd(NO_3)_2$ + 40% $(LiNO_3)_2$ → $(KNO_3)_2$. This also has four crystallization branches: cadmium nitrate, lithium nitrate, the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$, and potassium nitrate. The first transition point corresponds to a temperature of 186° and the composition: 5% potassium nitrate, 38% lithium nitrate, and 57% cadmium nitrate; the second corresponds to 141° and the composition: 40% potassium nitrate, 24% lithium nitrate, and 36% cadmium nitrate; the third corresponds to 140° and the composition: 55% potassium nitrate, 18% lithium nitrate, and 27% cadmium nitrate. The maximum corresponds to a temperature of 148° (Figure 4). The transition points are determined by the intersection of the crystallization curves and were experimentally confirmed. Vitrification was observed along the cadmium nitrate branch.

Section VI: 55% $Cd(NO_3)_2$ + 45% $(LiNO_3)_2$ → $(KNO_3)_2$. This section exhibits three crystallization branches: lithium nitrate, descending to 126°; the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$, and potassium nitrate. It has two transition points. The first corresponds to a temperature of 126° and the composition: 46% potassium nitrate, 24.5% lithium nitrate, and 29.5% cadmium nitrate; the second to 130° and the composition: 55% potassium nitrate, 20% lithium nitrate, and 25% cadmium nitrate.

The temperature corresponding to the maximum is 143° (Figure 5). Crystallization of the salts proceeded readily throughout the entire section.

Section VII: 45% $Cd(NO_3)_2$ + 55% $(LiNO_3)_2$ → $(KNO_3)_2$. There are two crystallization branches: lithium nitrate and potassium nitrate. The transition point is at 111° and corresponds to the composition: 55% potassium nitrate, 24.75% lithium nitrate, and 20.25% cadmium nitrate (Figure 5). No vitrification was observed throughout the whole of the section.

Section VIII: 35% $Cd(NO_3)_2$ + 65% $(LiNO_3)_2$ → $(KNO_3)_2$. There are two crystallization branches: lithium nitrate and potassium nitrate. The transition point corresponds to the composition: 56% potassium nitrate, 28.5% lithium nitrate, 15.5% cadmium nitrate, and a temperature of 115° (Figure 5). No vitrification was observed on any part of the line, and the salt melts crystallized normally.

Section IX: 20% $Cd(NO_3)_2$ + 80% $(LiNO_3)_2$ → $(KNO_3)_2$. In this case there are two crystallization branches: lithium nitrate and potassium nitrate. The transition point corresponds to the composition: 55% potassium nitrate, 36% lithium nitrate, and 9% cadmium nitrate, and the temperature of 117° (Figure 6). Crystallization proceeded readily throughout the curve.

Section X: 60% $Cd(NO_3)_2$ + 40% $(KNO_3)_2$ → $(LiNO_3)_2$. Two crystallization branches: the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$ and lithium nitrate. The transition point corresponds to a temperature of 138° and the composition: 33% potassium nitrate, 17.5% lithium nitrate, and 49.5% cadmium nitrate (Figure 6). No vitrification was observed.

Section XI: 55% $Cd(NO_3)_2$ + 45% $(KNO_3)_2$ → $(LiNO_3)_2$. Two crystallization branches: the chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$ and lithium nitrate. The transition point corresponds to the temperature of 140° and the composition: 35.75% potassium nitrate, 20.5% lithium nitrate, and 43.75% cadmium nitrate (Figure 6).

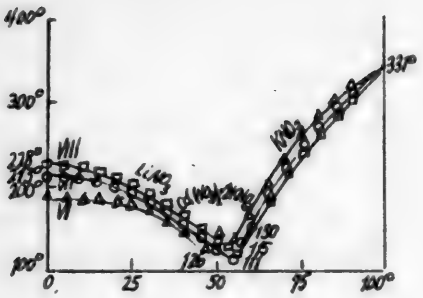

Fig. 5. VI) 55% $Cd(NO_3)_2$ + 45% $(LiNO_3)_2$ → $(KNO_3)_2$; VII) 45% $Cd(NO_3)_2$ + 55% $(LiNO_3)_2$ → $(KNO_3)_2$; VIII) 35% $Cd(NO_3)_2$ + 65% $(LiNO_3)_2$ → $(KNO_3)_2$.

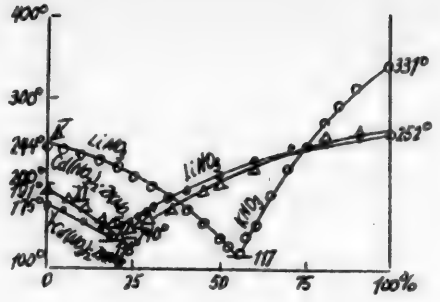

Fig. 6. IX) 20% $Cd(NO_3)_2$ + 80% $(LiNO_3)_2$ → $(KNO_3)_2$; X) 60% $Cd(NO_3)_2$ + 40% $(KNO_3)_2$ → $(LiNO_3)_2$; XI) 55% $Cd(NO_3)_2$ + 45% $(KNO_3)_2$ → $(LiNO_3)_2$.

No vitrification was observed. Section XI confirms the correctness of the course of the lines of common crystallization derived from the data of Sections III, IV, V, VI, VII.

The results of study of the ternary system are generalized in the projection of the triangle of isotherms of the three-dimensional phase diagram. The isotherms are drawn through 25° (Fig. 7).

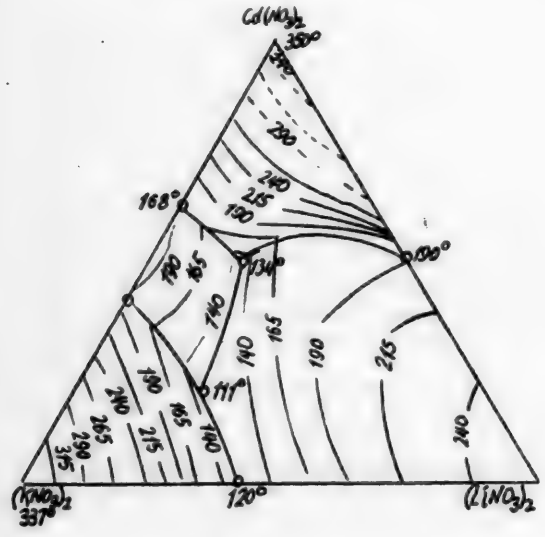

Fig. 7.

Figure 8 shows the orthogonal projection of the paths of crystallization. The composition and temperature of the invariant points obtained by the orthogonal projection of the curves of common crystallization on the cadmium nitrate– potassium nitrate side are in accord with the experimental data.

In the ternary system of the nitrates of lithium, potassium and cadmium, the liquidus surface was investigated. It was established that the system has four fields of crystallization: those of cadmium nitrate, lithium nitrate and the complex compound $Cd(NO_3)_2 \cdot 2KNO_3$. The two binary systems constituting the sides of the ternary system form simple eutectics, while on the third binary system (also forming a side of the triangle) exists the congruent chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$. The composition and temperature of the ternary eutectic points were determined experimentally. This system is characterized by an exceptionally low melting point of the ternary invariant point (a temperature of 111°), and by the presence of a well-defined complex between the nitrates of cadmium and potassium both in the binary system and in the presence of the third component. The formation of the complex compound $Cd(NO_3)_2 \cdot 2KNO_3$ is accompanied by a rise in the viscosity of the salt melts which in turn promotes formation of highly dispersed crystals and hinders observation of the development of the first crystals.

The supercooling of the salt melts, which had been observed with certain concentrations of components, facilitated the formation of a low-melting vitreous mass constituting the simplest nitrate glasses. A similar phenomenon was described by the author when examining the ternary system of the nitrates of calcium, potassium and sodium [3]. Vitrification has also been observed by N.P.Luzhna [4] in a study of the prism of the six salts Na, K, Zn, || SO_4, Cl.

The problem of the transformation of certain easily fusible salts into glassy modifications and the associated phenomenon of supercooling have not yet been adequately investigated and further research in this field is required. The treatment of these phenomena in the literature [5,6,7] in our opinion is open to question. From this standpoint our investigation deserves attention both in the theoretical and the practical respect.

SUMMARY

1. The ternary system $Cd(NO_3)_2-(KNO_3)_2-(LiNO_3)_2$ has been studied by the visual-polythermic method of physico-chemical analysis.

2. The ternary system in question is found to belong to the type of ternary systems with two invariant points. Corresponding to the first ternary invariant point is the composition: 32 mole % potassium nitrate, 17 mole % lithium nitrate, 51 mole % cadmium nitrate and a melting point of 134°. To the second invariant point corresponds the composition: 55 mole % potassium nitrate, 24.75 mole % lithium nitrate, 20.25 mole % cadmium nitrate and a melting point of 111°.

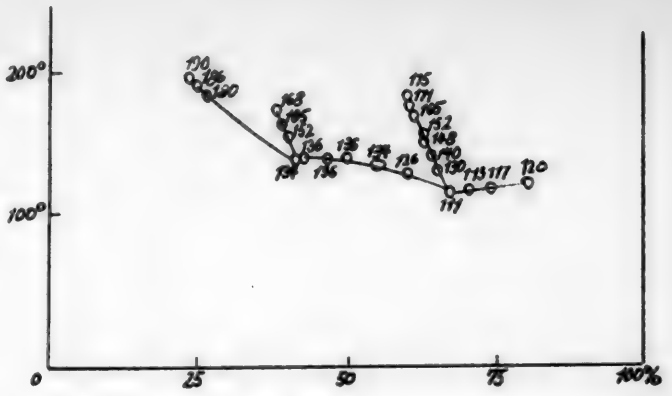

Fig. 8.

3. A study was made of the binary system of the nitrates of cadmium and potassium. This is a system with a maximum point to which corresponds the congruent chemical compound $Cd(NO_3)_2 \cdot 2KNO_3$ with melting point 199.5°.

The first eutectic corresponds to the composition: 38 mole % $(KNO_3)_2$ and 62 mole % $Cd(NO_3)_2$ and a temperature of 168°; to the second corresponds the composition: 60 mole % $(KNO_3)_2$, 40 mole % $Cd(NO_3)_2$ and a temperature of 175°.

4. Potassium nitrate differs from the nitrates of lithium and sodium in forming with cadmium nitrate the complex compound $Cd(NO_3)_2 \cdot 2KNO_3$.

5. It is shown that the introduction of cadmium and potassium ions into salt melts promotes the formation of nitrate glasses of the simplest chemical composition. This is a discovery of undoubted interest.

LITERATURE CITED

[1] P.I.Protsenko. J. Gen.Chem., 21, 1307(1952); see Consultants Bureau translation, p. 1351.

[2] Carveth. Handbook of Physico-chemical and Technological Values, Vol. 6, 174. Moscow (1931).

[3] P.I.Protsenko and A.G.Bergman. J.Gen.Chem., 20, 1365 (1950); see Consultants Bureau trans., p. 1421.

[4] N.P.Luzhnaya et al. Abstracts of Scientific Researches for 1944. Acad.Sci.USSR., Div.Chem.Sci., 42. Moscow-Leningrad (1945).

[5] A.A.Lebedev. Bull.Sect.Phys.Chem., Anal.Inst.Org.-Inorg.Chem., 16, No. 4, 6-52 (1945).

[6] G.Tamman. Krystallisieren und Schmelzen, 13-27, Leipzig (1903).

[7] G.Tamman. The Vitreous State. Moscow-Leningrad, 7-14 (1935).

Received December 29, 1950.

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THE EQUILIBRIUM IN THE RECIPROCAL SYSTEM OF THE SULFATES AND MOLYBDATES OF SODIUM AND LEAD

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This paper contains the results of an investigation of the fusibility in the ternary reciprocal system of the sulfates and molybdates of sodium and lead by the visual-polythermal method. The salts and their mixtures were melted in a platinum crucible. A resistance-wound crucible furnace of IONKh Alloy No.2* was employed. Temperatures were measured with a platinum – platinum-rhodium thermocouple and with a galvanometer calibrated for the melting points of chemically pure KNO_3, $K_2Cr_2O_7$, Na_2SO_4, KCl, and K_2SO_4. The sodium sulfate was purified by three recrystallizations and had a melting point of 884°; the sodium molybdate was prepared by recrystallization of commercial salt and melted at 698°; lead sulfate and molybdate were prepared by precipitation from solutions of lead nitrate and, respectively, sodium sulfate and sodium molybdate.

TABLE 1

Fusibility of the System $Na_2MoO_4 - PbMoO_4$

No.	$PbMoO_4$ (%)	Temp. of formation of the first crystals
1	0.0	690
2	2.5	721
3	5.0	695
4	10.0	687
5	15.0	681
6	20.0	666
7	22.5	654
8	25.0	644
9	27.5	630
10	30.0	635
11	35.0	676
12	40.0	714
13	45.0	749
14	50.0	784
15	55.0	823
16	60.0	860

TABLE 2

Diagonal Section of $Na_2MoO_4 - PbSO_4$

No.	$PbSO_4$ (%)	Temp. at start of crystallization
1	0.0	690
2	5.0	690
3	10.0	679
4	15.0	666
5	20.0	657
6	25.0	688
7	30.0	758
8	35.0	820
9	40.0	865
10	45.0	898
11	50.0	926
12	55.0	934
13	60.0	943
14	65.0	939
15	70.0	930
16	75.0	899
17	80.0	926

Binary Systems

The binary system sodium sulfate — sodium molybdate, previously described by Boeke [4], was again investigated in our laboratory. The system is characterized by a continuous series of solid solutions which decompose in the solid state under the influence of polymorphic transformations of the components.

The binary system lead sulfate – sodium molybdate has been studied by Ayre and Herms [4]. Limiting solid solutions were observed in the system in the regions adjoining the pure components which form a eutectic at 962° and 42.5% lead sulfate.**

The system of the sulfates of sodium and lead has been studied by Cagliani and Marotta [4]; it is characterized by a simple eutectic at 735° and 47% $PbSO_4$. The results are confirmed by our own experiments (Figure 1).

The binary system of the molybdates of sodium and lead had not previously been studied. Our results are presented in Table 1 and Figure 1. A simple eutectic was observed at 620° and 28% lead sulfate.

The reciprocal system was completely characterized by a study of the diagonal sections and of 10 internal sections. The distribution of the sections is shown in Figure 2.

The diagonal section of $Na_2MoO_4 - PbSO_4$ (Table 2 and Figure 1) has three crystallization branches which intersect at 650° and 23% lead sulfate and at 860° and 79% lead sulfate. The lead molybdate branch has a well-defined maximum at 944° and 60% lead sulfate. The diagonal section of sodium sulfate and lead molybdate clearly exhibits the character of a binary system with a saddle in the region of 50-70% lead molybdate and a eutectic point at 12.5% lead molybdate and 860°.

The fusibility data are presented in Table 3 and Figure 1.

The data for sections I to X are presented in Tables 4-13 and Figures 3-4.

* Institute of General and Inorganic Chemistry.

** Throughout the paper the percentages will be given as mole %.

TABLE 3

Diagonal Section of Na_2SO_4–$PbMoO_4$

No.	$PbMoO_4$ (%)	Temp. at start of crystallization
1	0.0	884
2	5.0	879
3	10.0	870
4	15.0	861
5	17.5	863
6	20.0	867
7	25.0	875
8	30.0	885
9	35.0	897
10	40.0	909
11	45.0	916
12	50.0	923
13	55.0	928
14	60.0	931
15	65.0	940
16	70.0	960
17	75.0	980
18	80.0	999

TABLE 4

Section I (25% Na_2SO_4, 75% Na_2MoO_4 + $PbSO_4$)

No.	$PbSO_4$ (%)	Temp at start of crystallization
1	0.0	700
2	5.0	695
3	10.0	691
4	15.0	704
5	20.0	740
6	25.0	782
7	30.0	834
8	35.0	878
9	40.0	906
10	45.0	924
11	50.0	934
12	55.0	936
13	60.0	931
14	65.0	919
15	70.0	895
16	75.0	867
17	80.0	958

TABLE 5

Section II (60% Na_2SO_4, 40% Na_2MoO_4 + $PbSO_4$)

No.	$PbSO_4$ (%)	Temp. at start of crystallization
1	0.0	734
2	2.5	732
3	5.0	735
4	7.5	754
5	10.0	770
6	15.0	798
7	20.0	839
8	25.0	870
9	30.0	890
10	35.0	900
11	40.0	900
12	45.0	900
13	50.0	905
14	55.0	895
15	60.0	878
16	65.0	849
17	70.0	845
18	75.0	935

TABLE 6

Section III (75% Na_2SO_4, 25% Na_2MoO_4) + $PbSO_4$

No.	$PbSO_4$ (%)	Temp. at start of crystallization
1	0.0	800
2	2.5	799
3	5.0	811
4	7.5	823
5	10.0	833
6	15.0	849
7	20.0	860
8	25.0	869
9	30.0	880
10	35.0	884
11	40.0	884
12	45.0	878
13	50.0	868
14	55.0	854
15	60.0	814
16	65.0	837
17	70.0	897

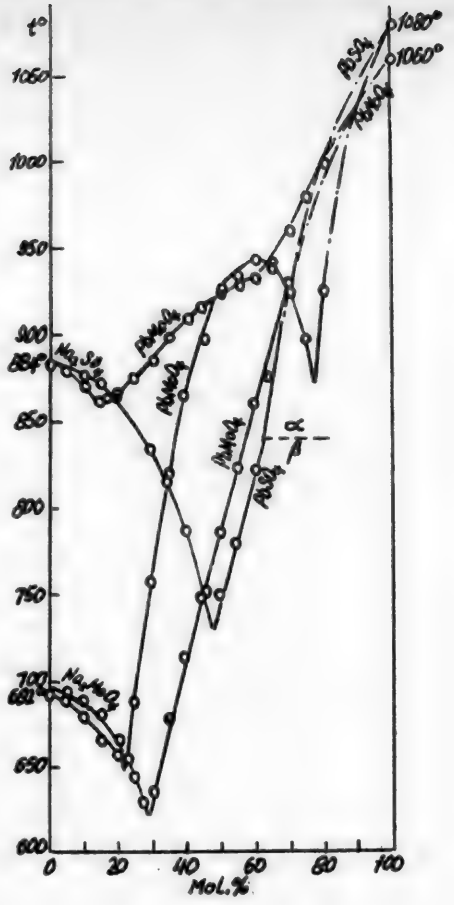

Fig. 1

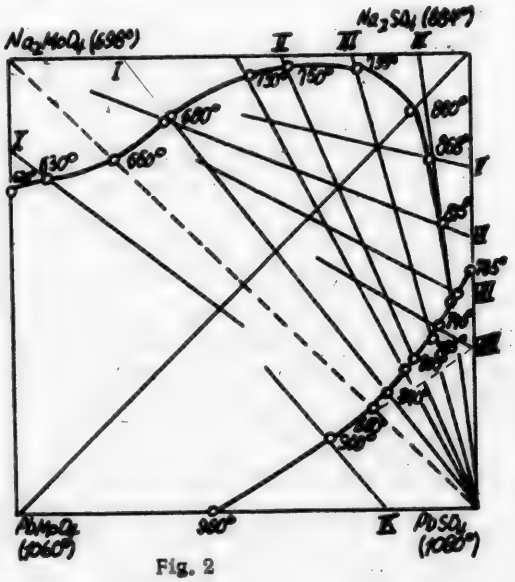

Fig. 2

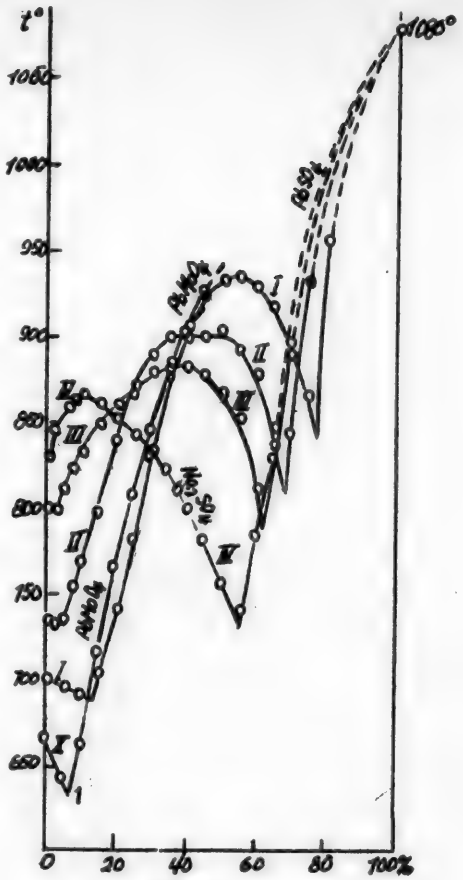

Fig. 3.

Fig. 4.

From the data of the diagonal and internal sections it has been possible to delineate in a square the reciprocal system of the field of crystallization of the individual salts (Fig. 5). The field of crystallization of lead molybdate occupies the greater part (74.88%) of the square; the field of crystallization of the solid solutions of the sulfate and molybdate of sodium occupy 13.78%; 11.40% in all belongs to the field of crystallization of lead sulfate, of which 9.77% belongs to the α- and 1.63% to the β-modification. One ternary eutectic point was detected in the system at 52% lead sulfate, 3.5% lead molybdate, 44.5% sodium sulfate and 730°; also one binary eutectic point lying on the stable diagonal of $Na_2SO_4 - PbMoO_4$ at 850° and 12.5% lead molybdate.

TABLE 7

Section IV (90% Na_2SO_4, 10% Na_2MoO_4) + $PbSO_4$

No.	$PbSO_4$ (%)	Temp. at start of crystallization	No.	$PbSO_4$ (%)	Temp. at start of crystallization
1	0.0	830	10	35.0	824
2	2.5	845	11	40.0	800
3	5.0	860	12	45.0	782
4	7.5	865	13	50.0	758
5	10.0	867	14	55.0	740
6	15.0	860	15	60.0	785
7	20.0	850	16	65.0	832
8	25.0	845	17	70.0	891
9	30.0	840			

Heat-of-formation data are not available for all of the components, and it is therefore not possible to calculate the thermal effect of the reaction:

$$Na_2SO_4 + PbMoO_4 \rightleftharpoons Na_2MoO_4 + PbSO_4.$$

However, it is clear from the character of the diagram that the equilibrium of the reciprocal reaction is shifted in the direction of linking of ions with radii of the same order of size (larger with larger, smaller with smaller, in accordance with the rules of Gustavson [5] and Beketov [6].)

On the basis of the classification of A. G. Bergman and N. S. Dombrovskaya [1-3] the system is an irreversible reciprocal one, although the presence of a saddle on the stable

TABLE 8

Section V (75% Na_2SO_4, 25% $PbSO_4$) + Na_2MoO_4

No.	Na_2MoO_4 (%)	Temp. at start of crystallization
1	0.0	862
2	2.5	861
3	5.0	857
4	7.5	854
5	10.0	856
6	12.5	856
7	15.0	860
8	20.0	860
9	25.0	850

TABLE 9

Section VI (60% Na_2SO_4, 40% $PbSO_4$) + Na_2MoO_4

No.	Na_2MoO_4 (%)	Temp. at start of crystallization
1	0.0	785
2	5.0	807
3	7.5	813
4	10.0	843
5	15.0	867
6	20.0	879
7	25.0	884
8	30.0	875
9	35.0	860
10	40.0	832
11	45.0	805
12	50.0	780
13	55.0	750
14	60.0	721
15	65.0	680
16	70.0	678

TABLE 10

Section VII (45% Na_2SO_4, 55% $PbSO_4$) + Na_2MoO_4

No.	Na_2MoO_4 (%)	Temp. at start of crystallization
1	0.0	783
2	2.5	755
3	5.0	753
4	7.5	810
5	10.0	833
6	15.0	872
7	20.0	890

TABLE 11

Section VIII (35% Na_2SO_4, 65% $PbSO_4$) + Na_2MoO_4

No.	Na_2MoO_4 (%)	Temp. at start of crystallization
1	0.0	866
2	2.5	826
3	5.0	800
4	7.5	780
5	10.0	809
6	15.0	860
7	20.0	883

TABLE 12

Section IX (20% $PbMoO_4$, 80% $PbSO_4$) + Na_2MoO_4

No.	Na_2MoO_4 (%)	Temp. at start of crystallization
1	0.0	—
2	10.0	960
3	12.5	902
4	15.0	910
5	20.0	930
6	25.0	950

TABLE 13

Section X (80% Na_2MoO_4, 20% $PbMoO_4$) + $PbSO_4$

No.	$PbSO_4$ (%)	Temp. at start of crystallization
1	0.0	665
2	5.0	642
3	10.0	662
4	15.0	717
5	20.0	767
6	25.0	809
7	30.0	846
8	35.0	883
9	40.0	909
10	45.0	927

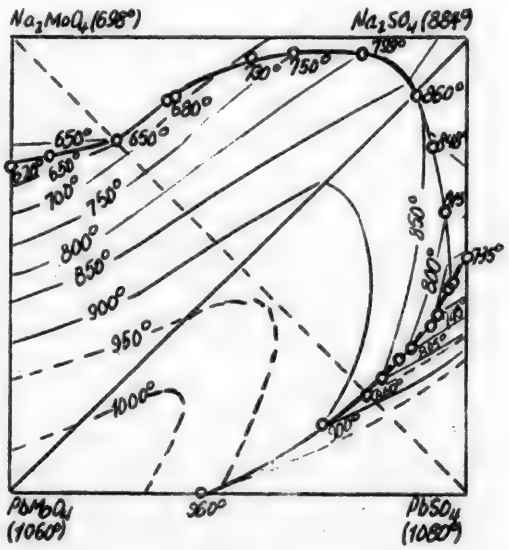

Fig. 5.

Na_2SO_4–$PbMoO_4$ section and the character of the isotherms in the field of crystallization of lead molybdate (displacement of the crest in the direction of lead sulfate) indicate some reversibility of the reaction at high temperatures.

SUMMARY

1. The ternary reciprocal system of the sulfates and molybdates of sodium and lead was investigated by the visual-polythermal method of physicochemical analysis.

2. According to the classification of A. G. Bergman and N. S. Dombrovskaya, the system is of the irreversible-reciprocal type with the stable diagonal Na_2SO_4–$PbMoO_4$.

LITERATURE CITED

[1] A. G. Bergman and N. S. Dombrovskaya, J. Russ. Chem. Soc. 61, 1451 (1920).

[2] E. I. Banashek and A. G. Bergman, Proc. Acad. Sci. USSR, LVI, 485 (1947).

[3] A. G. Bergman and G. A. Bukhalova, Bull. Sector Phys. Chem. Analysis, 33 (1949).

[4] See: Technical Encyclopedia. Handbook of Chemical, Physical and Technological Values, , Vol. VI.

[5] G. G. Gustavson, J. Russ. Chem. Soc. 5, 8, 357 (1873).

[6] N. P. Beketov and V. N. Beketov. On the reciprocal exchange of halides in the fused state. St. Petersburg (1903).

Received March 20, 1950

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THERMODYNAMICS OF THE KETONIZATION OF ETHYL ALCOHOL

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Over certain dehydrogenation catalysts primary alcohols pass through a series of consecutive reactions to form ketones as final products. This so-called ketonization of primary alcohols [1] has chiefly been studied in relation to ethyl alcohol. The reaction mechanism is complicated and is not altogether clear. The most probable scheme is that put forward in 1935 by M. Ya. Kagan, G. D. Lyubarsky and L. A. Sobolev [2], according to which the process successively involves: 1) Dehydrogenation of the alcohol to aldehyde; 2) ester-condensation of the aldehyde; and 3) ketonic cleavage of the ester. The complexity of the ketonization mechanism will also be realized when we recall that even the mechanism of ester formation from alcohols (i.e. the first two stages of the present reaction) has continued until recently to be the subject of investigations and discussions [1,3]. In the temperature range of 250-450° in which ketonization proceeds [1], certain reactions (which appear to be intermediate stages) are substantially reversible, and this fact must be kept in mind during the investigation of the mechanism and kinetics of the reaction. In consequence it is important to have data for the equilibria of the series of reactions taking place under ketonization conditions, for otherwise it would be difficult to demarcate the kinetic and thermodynamic factors when changes occur in the temperature regime.

We are concerned with the equilibria of the following reactions:

$C_2H_5OH \rightleftarrows CH_3CHO + H_2$ (I) — dehydrogenation of ethyl alcohol,
$2CH_3CHO \rightleftarrows CH_3COOC_2H_5$ (II) — ester-condensation of acetaldehyde (Tishchenko's reaction),
$2CH_3COOC_2H_5 \rightleftarrows CH_3COCH_3 + C_2H_4 + CO_2 + C_2H_5OH$ (III) — ketonic cleavage of ethyl acetate,
$3C_2H_5OH \rightleftarrows CH_3COCH_3 + C_2H_4 + CO_2 + 4H_2$ (IV) — overall reaction of ketonization of ethyl alcohol,
$2C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + 2H_2$ (V) — reaction of esterification (acidless) of ethyl alcohol,
$3CH_3CHO \rightleftarrows CH_3COCH_3 + C_2H_4 + CO_2 + H_2$ (VI) — reaction of ketonization of acetaldehyde.

Data for the thermodynamics of reaction (V) were published in 1949 by Vvedensky and co-workers [4]. In the present paper we have calculated the equilibria of the remaining five reactions, using the literature data published in the past ten years (Table 1). In the cases which could be verified, the calculated data agreed with the experimental.

The Reaction of Ethyl Alcohol Dehydrogenation

Since Rideal's data [12], in connection with a study of the equilibrium in the range 150-275°, cannot be considered sufficiently accurate [11], the equilibrium has been calculated on the basis of the third law, using the experimentally determined value of the thermal effect of the reaction: $\Delta H_{298} = 16752$ cal/mole [13].

The calculation, both in the present case and in the others, was performed according to the following scheme:

1. From the data of Table 1 the equation correlating the difference between the heat capacities of the reaction products and the starting products was calculated:

$$\Delta C_p = \Delta\Gamma_0 + \Delta\Gamma_1 T + \Delta\Gamma_2 T^2. \qquad (1)$$

2. From the equation:

$$\Delta H_T = \Delta H_0 + \Delta\Gamma_0 T + \frac{\Delta\Gamma_1}{2} T^2 + \frac{\Delta\Gamma_2}{3} T^3 \qquad (2)$$

the magnitude ΔH_0 was calculated.

For the reaction in question the experimental value of ΔH_{298} was inserted in equation (2); in the remaining cases the value ΔH_{298} determined according to Table 1 was taken.

3. From the equation

$$\Delta Z = \Delta H - T\Delta S \qquad (3)$$

TABLE 1

Thermodynamic Functions of Participants in the Reactions

Compounds (gas)	Heat of formation ΔH^0_{298}	Entropy S_{298}	Equations relating specific heat (C_p) to temp. (°K)	Temp. interval (°K)**
Ethyl alcohol	−56240 [5]	67.26 [6]	$5.5656 + 0.04522T - 0.00001639T^2$ [4]	300-700
Acetaldehyde	−39670 [7]	63.15 [7]	$2.97 + 0.03727T - 0.00001339T^2$*	300-1000
Ethyl acetate	−103444 [4]	90.11 [4]	$2.27 + 0.088T - 0.00003086T^2$ [4]	300-700
Acetone	−57790 [8]	70.3 [9]	$5.37 + 0.048227T - 0.000015182T^2$[10]	298-1500
Ethylene	12496 [11]	52.45 [11]	$2.08 + 0.0311T - 0.00001066T^2$[11]	300-1500
Carbon dioxide	−94052 [11]	51.06 [11]	$5.372 + 0.12404T - 0.00000478T^2$[11]	300-1500
Hydrogen	0	31.21 [5]	$6.744 + 0.0002774T + 0.0000001956T^2$[5]	300-1500

was determined the value ΔZ^0_{298}. ΔS^0_{298}. Calculation of the value was effected from the data of Table 1.

4. The magnitude of I was calculated by substituting the values ΔZ^0_{298} and ΔH^0_{298}

$$\Delta Z_T = \Delta H_0 - \frac{\Delta\Gamma_0}{0.4343} T \log - \frac{\Delta\Gamma_1}{2} T^2 - \frac{\Delta\Gamma_2}{6} T^3 + IT \quad (4)$$

5. The final equation for the temperature-dependence of log K_p was obtained by substituting the experimental values in the equation:

$$\log K_p = -\frac{\Delta H_0}{4.573} + \frac{\Delta\Gamma_0}{1.986} \log T + \frac{\Delta\Gamma_1}{2.4573} T + \frac{\Delta\Gamma_2}{6 \cdot 4.573} T^2 - \frac{I}{4.573}. \quad (5)$$

The following was found for reaction (I): $\Delta C_p = 4.1484 - 0.007673T + 0.000003196\ T^2$; $\Delta H_0 = 15714$ cal/mole; $\Delta H_{298} = 16637$ cal/mole; $\Delta Z^0_{298} = 8561$ cal/mole; $I = -1.468$.

$$\log K_p = -\frac{3436}{T} + 2.0886 \log T - 0.0008386\ T + 0.0000001166\ T^2 + 0.3210 \quad (6)$$

In Table 2 are presented by comparison the experimental data for log K_p [12] and those calculated according to equation (6).

TABLE 2

Comparison of log K_p, calculated from equation (6) with the calculated and experimental data of Rideal [12]

t° C	T°K	log K_p (exp.)	log K_p (Eq.(6))
150	423	−2.796	−2.651
175	448	−2.322	−2.164
200	473	−1.917	−1.727
225	498	−1.345	−1.334
250	523	−0.635	−0.981
275	548	−0.041	−0.653

The Ester-Condensation Reaction (V.E. Tishchenko's Reaction)

$$2CH_3CHO \rightleftharpoons CH_3COOC_2H_5$$

The expression for the equilibrium constant of this reaction can be derived from the equilibrium constants of the dehydrogenation reaction (I) and of the reaction of esterification in absence of acid (V):

$$K_{p(II)} = \frac{P_{CH_3COOC_2H_5}}{P^2_{CH_3CHO}} = \frac{K_{p(V)}}{K^2_{p(I)}} \quad (7)$$

From this it follows that:

$$\log K_{p(II)} = \log K_{p(V)} - 2 \log K_{p(I)}. \quad (8)$$

On the basis of experimental data A. A. Vvedensky and co-workers [4] proposed the following equation:

$$\log K_{p(V)} = -\frac{1675.7}{T} + 2.33 \log T - 0.0002061\ T + 0.000000084\ T^2 - 2.3929 \quad (9)$$

Combining equations (6) and (9) in accordance with (8), we get:

$$\log K_{p(II)} = \frac{5196}{T} - 1.847 \log T + 0.001471\ T - 0.000000149\ T^2 - 3.0349. \quad (10)$$

* The equation for the specific heat of acetaldehyde was calculated (V.M.) on the basis of the data of Pitzer and Weltner [7] by the method of least squares.

** In this column are listed the temperature ranges put forward for the specific heat equation.

TABLE 3

Comparison of log K_p, calculated from equation (10) with the values calculated from the data of A. A. Vvedensky and co-workers

t° C	T° K	From data of A. A. Vvedensky and co-workers [4]	log K_p from Equation (10)
181	454	4.658	4.140
181	454	4.565	4.140
201.5	474.5	3.662	3.637
201.5	474.5	4.041	3.637

Although there are no papers in the literature on the experimental investigation of the equilibrium of the reaction of ester-condensation of acetaldehyde, for the purpose of comparing the values of log K_p calculated from equation (10) with the experimental data, we may utilize the data given in the paper of A. A. Vvedensky and co-workers devoted to a study of the equilibrium of acidless esterification [4]. Since the aldehyde is an intermediate in the reaction of acidless esterification, its concentration after establishment of equilibrium between alcohol on the one hand and the ester and hydrogen on the other hand will also be an equilibrium concentration. Unfortunately, the concentration of the aldehyde under the conditions described by the authors of the experiments is extremely small (several tenths wt. %), so that even a small absolute error in its determination would introduce a large error into the calculation of the equilibrium constant of reaction (II). The data used in the calculation were taken from those experiments on whose basis the authors derived the equation for the equilibrium constant of the reaction of acidless esterification (Table 3).

Equation (10) permits calculation of ΔH_{298} and ΔZ^0_{298} of the reaction:

$$\Delta H_{298} = -24290 \text{ cal/mole. } \Delta Z^0_{298} = -13980 \text{ cal/mole.}$$

Ketonization of Ethyl Acetate

$$2CH_3COOC_2H_5 \rightleftharpoons CH_3COCH_3 + C_2H_4 + CO_2 + C_2H_5OH \text{ (III)}$$

The following values are found from the data of Table 1: $\Delta H_{298} = 17300$ cal/mole; $\Delta Z^0_{298} = -840$ cal/mole; $\Delta C_p = 12.848 + 0.0726\ T + 0.00001471\ T^2$; $\Delta H_0 = 10114$ cal/mole; I = 47.494.

$$\log K_{p(III)} = -\frac{2212}{T} + 6.469 \log T + 0.007938\ T + 0.0000005358\ T^2 - 10.386. \qquad (11)$$

Ketonization of Ethyl Alcohol

$$3C_2H_5OH \rightleftharpoons CH_3COCH_3 + C_2H_4 + CO_2 + 4H_2 \text{ (IV)}$$

$\Delta H_{298} = 35374$ cal/mole; $\Delta Z^0_{298} = 6497$ cal/mole; $\Delta C_p = 23.101 + 0.06882\ T + 0.00001933\ T^2$; $\Delta H_0 =$

$= 25259$ cal/mole; I = 79.225.

$$\log K_{p(IV)} = -\frac{5523}{T} + 11.632 \log T + 0.007525\ T + 0.0000007041\ T^2 - 17.325 \qquad (12)$$

Ketonization of Acetaldehyde

$$3CH_3CHO \rightleftharpoons CH_3COCH_3 + C_2H_4 + CO_2 + H_2 \text{ (VI)}$$

$\Delta H_{298} = -14336$ cal/mole; $\Delta Z^0_{298} = -18977$ cal/mole; $\Delta C_p = 10.656 + 0.09183\ T + 0.00000974\ T^2$;

$\Delta H_0 = -21679$ cal/mole; I = 83.649.

$$\log K_{p(VI)} = \frac{4741}{T} + 5.366 \log T + 0.01004\ T + 0.0000003549\ T^2 - 18.292 \qquad (13)$$

In Table 4 are presented the values of log K_p of reactions I-VI calculated from the above equations.

The calculations enable the following conclusions to be drawn:

1) The mechanism of the ketonization of ethyl alcohol proposed by M. Ya. Kagan and co-workers is thermodynamically probable in all its stages.

2) In the temperature range 250-450° (in which the ketonization was effected [1])the reactions of ketonization of alcohol, aldehyde and ester are substantially irreversible.

3) The temperature of 250° is not the bottom limit for the ketonization of alcohol, aldehyde and ester. By choosing suitable catalysts it is possible to effect these reactions at lower temperatures.

TABLE 4

log K_p of Reactions I-VI calculated from the Respective Equations

Reaction	250° C	300° C	350° C	400° C	450° C
$C_2H_5OH \rightleftharpoons CH_3CHO + H_2$ (I)	−0.981	−0.357	0.165	0.611	0.995
$2CH_3CHO \rightleftharpoons CH_3COOC_2H_5$ (II)	2.610	1.733	1.003	0.385	−0.143
$2CH_3COOC_2H_5 \rightleftharpoons CH_3COCH_3 + C_2H_4 + CO_2 + C_2H_5OH$ (III)	7.259	8.321	9.295	10.205	11.071
$3C_2H_5OH \rightleftharpoons CH_3COCH_3 + C_2H_4 + CO_2 + 4H_2$ (IV)	7.775	9.663	11.277	12.747	14.102
$2C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + 2H_2$ (V)	0.649	1.020	1.333	1.605	1.846
$3CH_3CHO \rightleftharpoons CH_3COCH_3 + C_2H_4 + CO_2 + H_2$ (VI)	10.701	10.652	10.706	10.846	11.052

4) In kinetic studies of the ketonization reaction, account should be taken of the reversibility of reactions I (dehydrogenation of alcohol), II (ester-condensation of aldehyde) and III (acidless esterification of alcohol). Knowledge of the velocity constants of these reactions provides the possibility of determination of the distance of the reacting system from the equilibrium point, and of ascertaining which reaction governs the velocity of the overall reaction.

SUMMARY

On the basis of thermodynamic data published in the literature of the past ten years, equations are derived for the temperature dependence of the logarithm of the equilibrium constants of the following reactions: 1) Dehydrogenation of ethyl alcohol; 2) ester-condensation of acetaldehyde (V. E. Tishchenko's reaction); 3) ketonization of ethyl acetate; 4) ketonization of ethyl alcohol; 5) ketonization of acetaldehyde.

It is shown that in the experimentally established temperature range of ketonization of 250-450°, the last three reactions are substantially irreversible.

The author expresses his sincere gratitude to A. A. Vvedensky for a number of valuable observations.

LITERATURE CITED

[1] B. N. Dolgov, Catalysis in Organic Chemistry, State Chemical Press (1949).

[2] M. Ya. Kagan, I. A. Sobolev and G. D. Lyubarsky, Ber. 68, 1140 (1935).

[3] B. N. Dolgov and T. V. Nizovkina, J. Gen. Chem. 19, 1125 (1949). *

[4] A. A. Vvedensky, P. Ya. Ivannikov and V. A. Nekrasova, J. Gen. Chem., 19, 1094 (1949). **

[5] M. Moskow, J. G. Aston, J. Res. Nat. Bur. Standards, 77, 263 (1946).

[6] J. G. Aston, Ind. Eng. Chem. 34, 514 (1942).

[7] K. S. Pitzer, W. Weltner, J. Am. Chem. Soc. 71, 2842 (1949).

[8] C. B. Miles, H. Hunt, J. Phys. Chem. 45, 1346 (1941).

[9] J. G. Aston, J. Chem. Phys. 12, 336 (1944).

[10] M. Kh. Karapetyants. Chemical Thermodynamics. State Chemical Press (1949).

[11] A. A. Vvedensky, Thermodynamic Calculations of the Processes of the Fuel Industry. State Fuel-Technical Press (1949).

[12] E. K. Rideal, Proc.Roy.Soc., 88A, 133 (1921).

[13] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, W. E. Waughan, J. Am. Chem. Soc., 60, 440 (1938).

Received December 19, 1950.

* See Consultants Bureau translation, p. 1119.

** See Consultants Bureau translation, p. 1087.

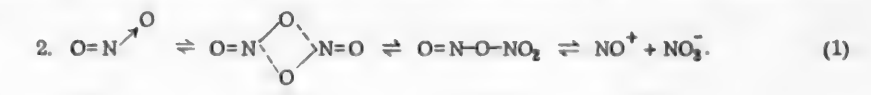
THE MECHANISM OF REACTION OF NITROGEN DIOXIDE WITH AROMATIC HYDROCARBONS

A. I. Titov

The problem, important in itself, of the mechanism of the reaction of nitrogen dioxide with the nuclei of aromatic compounds has acquired even greater theoretical significance following our discovery that the nitration of aromatic compounds (including hydrocarbons) by nitric acid, up to a concentration of acid characteristic of each substance, proceeds through intermediate interaction with nitrogen dioxide [1]. The clarification of the process is made difficult by a series of factors, namely: the complexity of the molecular composition of nitrogen dioxide itself, the formation in the sphere of reaction of other oxy compounds of nitrogen (NO, N_2O_3, HNO_2, HNO_3, etc), the presence of free oxygen, the diversity of products formed, and the inadequacy with which they have been studied.

Among the experimental data on the action of nitrogen dioxide on aromatic hydrocarbons, great interest is presented by the numerous observations of the smooth transformation of naphthalene into α-nitronaphthalene. In contrast to this, Wieland [2] found that the heating in a sealed tube at 80° of an equimolecular mixture of benzene and N_2O_4 gave, apart from nitrobenzene, a considerable amount of trinitrobenzene and picric acid. Attention is also merited by the work of Meisenheimer [3] and Schmidt [4] on the formation of addition products of oxides of nitrogen with anthracene and phenanthrene in the 9,10-position.

In our opinion nitrogen dioxide constitutes an equilibrium system of the following components:



(A) (B) (C) (D) (1)

The dimeric form (B) is stable in a nonpolar medium at low temperatures; rise of temperature and of the degree of dilution leads to breakdown to molecules of NO_2. An increase in the polarity of the medium and of its dissociative power will favor the development of the nitrosyl-nitrate form (C) and of its ionization with formation of the nitrosyl cation NO^+ (D); the latter process should be very strongly promoted by the presence of hydrogen or "aprotonic" acids which combine with the nitrate ion, for example, very concentrated nitric acid:

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

$$NO_3^- + H^+ \longrightarrow HNO_3 \text{ or } NO_3^- + HNO_3 \rightleftharpoons NO_3^- \ldots HNO_3. \qquad (2)$$

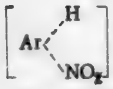
Reaction of N_2O_4 with sulfuric acid and similar strong acids leads to formation of the nitrosyl cation NO^+ and the nitronium cation NO_2^+.

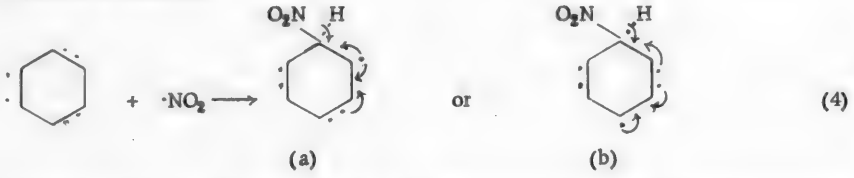
On the basis of the above facts, it is assumed in our theory that the active agent during nitration in a nitric acid medium is the nitrosyl cation NO^+, in sulfuric acid it is the nitronium cation NO_2^+, and in a nonpolar medium it is predominantly the monomer of nitrogen dioxide. All of these agents possess a low electron potential (P_{NOX} [1]) and accessibility of their electrophilic nitrogen atoms.

We have now collected a good deal of evidence in support of our theory that, as a rule, the initial stage in the interaction of oxides of nitrogen with aromatic hydrocarbons in large excess is the reaction with monomeric nitrogen dioxide. In agreement with the above theory we observed (see Experiment 1) a very large increase in the overall yields of products of reaction of the same quantity of nitrogen dioxide with benzene with increasing amount of hydrocarbon. The yield-improving effect of dilution, which is contrary to theory, may be accounted for by the decline in the inhibiting action of nitric oxide due to the displacement of the equilibrium to the left:

$$NO + NO_2 \rightleftharpoons N_2O_3. \qquad (3)$$

Further evidence that the active agent is NO_2 is provided by our observations on the possible realization of the reaction at 100-150° and with high dilution with the hydrocarbon, i.e. under conditions of substantially complete dissociation of N_2O_4 (Experiment 3). In harmony with our conclusion we observed a sharp acceleration of the reaction of nitrogen dioxide with benzene when saturated with oxygen (Experiment 2) which had the effect of breaking the bond of NO_2 with nitric oxide (see Equation 3). In this case, however, the manifestation was also possible of the specific action of the initial products of reaction of oxides of nitrogen with molecular oxygen.

According to our theory the reaction of NO_2 with the benzene ring leads to formation of the radical  , whose structure to a first approximation (allowing for the homolytic conjugation) can be represented by a structure of type (a) or type (b):

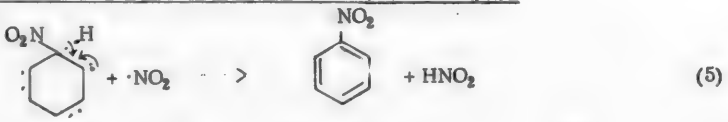


(4)

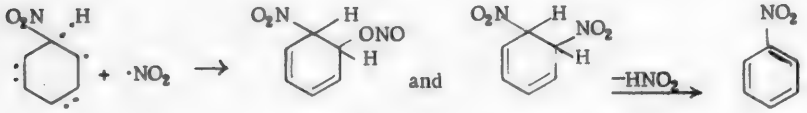
(the dots signify associated electron pairs participating in the conjugation). Heterolytic conjugation also no doubt takes place at the same time.

Among the products of reaction of nitrogen dioxide with benzene, we succeeded in separating nitrobenzene, m-dinitrobenzene, symm.-trinitrobenzene, p-dinitrobenzene, 2,4-dinitrophenol, and picric and oxalic acids. In the light of the foregoing exposition and of the inertness of nitrobenzene towards nitrogen dioxide under our experimental conditions, it may be permissible to represent the mechanism of their formation from the radicals (4) by the following schemes:

1. Formation of Nitrobenzene by Schemes (5) and (6):



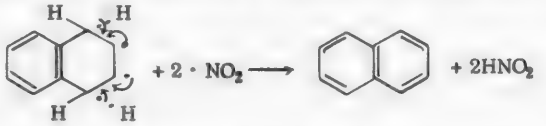
(5)



(6)

(a) (b)

Detachment of partly atomic hydrogen according to scheme (5) corresponds to the first stage of nitration of paraffins [5] $R{-}H + \cdot NO_2 \longrightarrow R + HNO_2$; but in this case instead of a free radical there is formed a stable molecule which also promotes the rapid course of the reaction without expenditure of energy of activation. This reaction is analogous to the dehydrogenation of hydroaromatic compounds by NO_2, for example dihydronaphthalene:

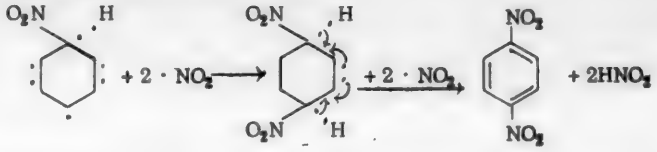


(7)

The ease of realization of such reactions reflects the strong tendency of these compounds to form aromatic nuclei (cryptoaromatic state).

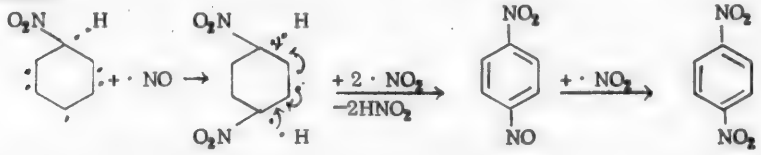
The formation of a mononitro derivative proceeds especially smoothly during reaction of NO_2 with naphthalene. When NO_2 reacts with anthracene and phenanthrene the process takes place according to scheme (6) and stops at stage (6a).

2. Formation of p-Dinitrobenzene:



(8)

It proceeds in a similar manner to the dehydrogenation of dihydronaphthalene in accordance with equation (7). It is quite likely that a portion of the p-dinitrobenzene is formed through the stage of addition of nitric oxide to the radical of (5), dehydrogenation of the adduct and oxidation of the resultant p-nitrosobenzene to the dinitro compound:

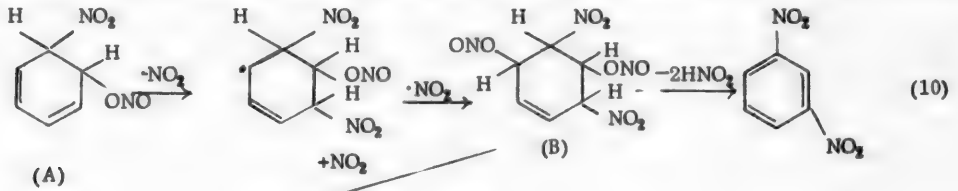


(9)

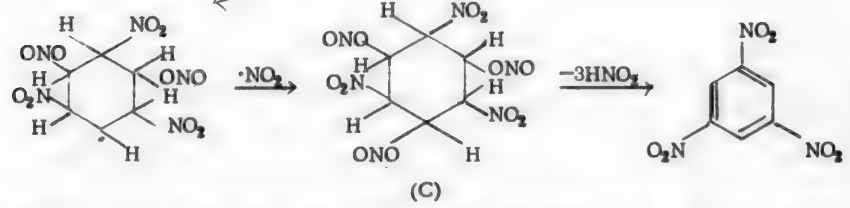
The still unisolated o-dinitrobenzene is undoubtedly also formed by this route.

3. Formation of m-Dinitrobenzene and symm.-Trinitrobenzene.

These are undoubtedly formed as a result of further addition of NO_2 to the intermediate product, cyclohexadiene [see, for example, schemes (6) and (8)] followed by cleavage of the elements of nitrous acid:



(10)

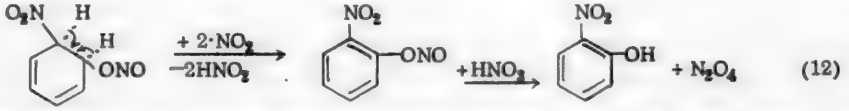


(11)

Some of our observations and those of Puranen [6] indicate the possible appearance among the reaction products of adducts of types (B) and (C).

4. Formation of Nitrophenols

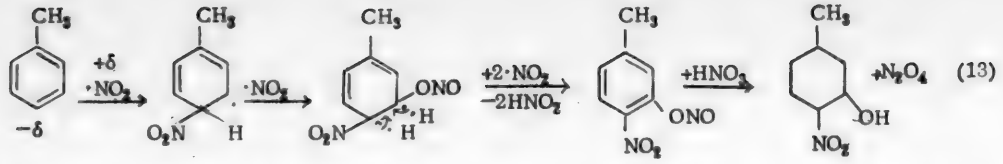
This proceeds through the stage of dehydrogenation of adducts (A), (B) and (C) [see equations (10) and (11)], for example according to the scheme:



(12)

The resultant nitrophenol is converted into dinitrophenols and picric acid by the mechanism which had been clarified in the preceding paper [1]. Dehydrogenation of the adducts (B) and (C) leads respectively to dinitrophenol and picric acid.

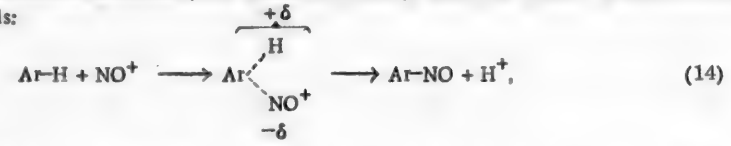
On the basis of the proposed mechanism the reaction of toluene with nitrogen dioxide should be expected to yield nitro derivatives of m-cresol, while in the case of the reaction of NO_2 with chlorobenzene we should expect nitro derivatives of m-chlorophenol, as can be seen, for example, from the following simplified scheme:



(13)

We have actually succeeded in demonstrating that trinitro-m-cresol is the chief component of the mixture of nitrocresols formed in the reaction of NO_2 with toluene, whereas the predominating product in the mixture of nitrocresols resulting from the nitration of toluene with strong nitric acid or sulfuric-nitric mixture is dinitro-p-cresol, probably in admixture with dinitro-o-cresol. We have likewise shown that in the nitration of chlorobenzene with nitrogen dioxide or aqueous nitric acid the mixture of nitrophenols mainly consists of nitro derivatives of m-chlorophenol; nitration with aqueous nitric acid proceeded to some extent through intermediate interaction with NO_2.

It must be pointed out that a certain number of the mononitro derivatives of p-dinitro compounds and of nitrophenols, including also anomalous members (e.g. trinitro-m-cresol), could be formed through intermediate formation of nitroso compounds:



(14)

whose transformation, according to our investigations [3], could likewise lead to the production of the cited compounds. Formation of m-dinitro compounds and of symm.-trinitro compounds could proceed exclusively by the previously mentioned route through the intermediate compound with NO_2.

The theory which has been developed of the interaction of aromatic hydrocarbons with oxides of nitrogen is applicable in large measure to the reactions of nitrogen oxides with olefins.

A large part of the present investigation was carried out in 1940-1941.

EXPERIMENTAL

1. Effect of dilution with hydrocarbon upon the yield of the reaction of nitrogen dioxide with benzene. Three mixtures of 10 ml nitrogen dioxide and 200 ml benzene were allowed to stand for 4 months at a temperature of about 20° in closed small bottles with volumes of, respectively, 40, 70 and 230 ml. The reaction mass in the first experiment had a green-brown color; the greenish tinge due to N_2O_3 in the second experiment was somewhat weaker, while in the third it was scarcely noticeable. A little oxalic acid separated out in each experiment. Picric acid was determined as potassium picrate which was obtained by treating the reaction mass with 10 ml of 10% $KHCO_3$ solution. The total yield of nitro- and polynitrobenzenes was determined by fractionation of the benzene in vacuum while heating on the water bath. Yields of the various products are summarized in the following table.

Expt. No.	Vol. of benzene	Yield		
		$H_2C_2O_4$ in g	picrate in g	nitro derivatives in g
1	20	0.29	0.31	0.26
2	50	0.34	0.60	0.87
3	200	0.68	0.95	2.6

2. Effect of presence of oxygen upon the interaction of nitrogen dioxide with benzene. A mixture of 100 ml benzene and 9.6 g nitrogen dioxide was allowed to stand under pressure of oxygen from a gasholder. The mixture was periodically shaken, sometimes while passing a stream of oxygen. At the end of 20 days the oxides of nitrogen had almost completely disappeared (compare expt. 4) The reaction mass was worked up to give 2.9 g picrate and 14.8 g nitrobenzene, the latter distilling without decomposition and almost without residue at 205-208°.

3. Interaction of nitrogen dioxide with benzene at 100° in sealed tubes with considerable dilution with hydrocarbon. Isolation of symm.-trinnitrobenzene. Into each of two sealed tubes (capacity about 100 ml) was charged 2 ml nitrogen dioxide and 15 ml benzene. The duration of heating in a horizontal water bath was 4 hours. Considerable pressure was manifested on opening

the tubes. Each of them was found to contain about 0.4 ml of aqueous layer with specific gravity 1.24. The hydrocarbon layer from both tubes was washed with water (10 ml) and then extracted with 20 ml of 5% caustic alkali solution. The aqueous layers and the extracts gave 0.14 g residue after evaporation. This residue consisted mainly of oxalic acid. The alkaline solution was acidified with hydrochloric acid and steam-distilled with a small volume of liquid in the distillation flask. From the residue in the flask (32 ml) was separated 0.29 g picric acid with m.p. 104-107°. This gave a rise in melting point when heated in admixture with an authentic specimen. The distillate after saturation with sodium chloride was extracted with ether. From the ether extract was obtained 0.05 g of 2,4-dinitrophenol, melting at about 105°.

The excess of hydrocarbon was distilled off in vacuum from the benzene layer after washing with water. The residue (1.24 g) was steam-distilled. From the distillate was separated about 1 g of liquid consisting mainly of nitrobenzene. The solid residue (0.15 g) from the distillation flask was crystallized from alcohol. The crystals obtained melted at 117-119°; in admixture with pure symm.-trinitrobenzene the melting point was 121-122°. The product gave all the reactions characteristic of symm.-trinitrobenzene, in particular the intense red coloration with caustic alkali solution.

4. Reaction of nitrogen dioxide with benzene at the ordinary temperature and pressure. Isolation of p-dinitrobenzene. A mixture of 500 ml benzene, 20 ml nitrogen dioxide and 2.1 g sodium nitrite was left to stand for six months (the cork was loosely inserted); a portion of the nitrogen dioxide did not enter into reaction. Extraction of the reaction mass with sodium bicarbonate solution gave 5.8 g picric acid; the caustic alkaline extract, following acidification and steam-distillation, yielded 0.5 g of 2,4-dinitrophenol with m.p. 106-109°. After distillation of the benzene (24.3 g) the residue was composed mainly of nitrobenzene. Steam-distillation of later fractions (i.e. after removal of the nitrobenzene) gave about 0.8 g of crystalline material. This crystallized from alcohol in the form of needlets melting at 168-170°. The melting point was elevated after mixing with pure p-dinitrobenzene. The identity of the product with p-dinitrobenzene was also confirmed by its conversion into p-nitrophenol when boiled with dilute caustic alkali.

5. Reaction of nitrogen dioxide with benzene at a temperature of 50-55° and at the ordinary pressure. Separation of m-dinitrobenzene. A mixture of 20 ml nitrogen dioxide, 930 ml benzene and 5 g anhydrous calcium nitrate was heated in a flask beneath a reflux condenser (ground-glass connection) for a period of 100 hours. The experiment was spread over 20 days. The reaction mass was worked up with water and after filtration gave 1.8 g calcium oxalate. On subsequent stirring with 100 ml of 10% potassium bicarbonate solution, a picrate was precipitated which yielded 4.6 g picric acid, m.p. 111-115°. Acidification of the mother liquor from the picrate followed by steam-distillation gave 0.35 g crystalline 2,4-dinitrophenol.

Benzene was distilled off in vacuum from the hydrocarbon layer. By means of combined distillation in steam and in vacuum the residue (6.95 g) gave 5.1 g nitrobenzene and 2.1 g m-dinitrobenzene in admixture with a little p-dinitrobenzene. Two crystallizations of the mixture of dinitrobenzenes (m.p. 70-100°) from alcohol gave a product melting at 82-84° which exhibited melting point elevation when mixed with pure m-dinitrobenzene. The residue of material nondistillable in steam (about 1.3 g) gave a definite reaction for symm-trinitrobenzene but the pure product could not be isolated.

In a similar experiment whose conditions were not precisely defined, steam-distillation of the mixture of dinitrobenzenes yielded a product with m.p. of about 130° from which p-dinitrobenzene was crystallized (from alcohol) with m.p. 161-165°.

6. Action of nitrogen dioxide on toluene in presence of oxygen. Isolation of trinitro-m-cresol and dinitro-p-cresol. A mixture of 2 l toluene, 10 ml nitrogen dioxide and 10 ml calcium nitrate was stood in a bottle under oxygen pressure with occasional shaking. Further addition was made of 6 ml nitrogen dioxide every two days. About 1.5 ml oxygen was absorbed each day; in addition 0.5 l oxygen was expended in driving out accumulated nitrogen and residual gases. After standing for 8 days the reaction mass was treated with water, and then, in succession, with 100 ml of 20% $KHCO_3$ solution and the same volume of 20% K_2CO_3 solution. The extraction with bicarbonate resulted in precipitation of 0.12 g crystals which on further treatment with hydrochloric acid yielded a substance melting at 85°. This was not examined closely. Inspissation of the solution on the water bath gave 1.05 g yellow crystalline salt. Acidification of the solution of the latter gave 0.8 g pure trinitro-m-cresol with m.p. 105° and depressing the melting point of an authentic specimen.

From the carbonate extract was obtained 0.26 g red crystalline precipitate which was worked up with acid to give dinitro-p-cresol, m.p. 80.5° (no depression of mixed melting point). Acidification of the mother liquors of both extracts led to the isolation of about 1 g of a liquid mixture of nitrocresols. The reaction mass was found to contain (using the previously described procedure [5]) 0.9 g of a mixture of o- and p-nitrotoluenes, over 50 g of methyl-substituted products (7 g phenylnitromethane, 29.6 g benzyl alcohol and its ethers, 7 g benzaldehyde, 2 g benzoic acid and 8 g of so-called residual oil). We have previously discussed the mechanism of formation of the latter [5,7].

SUMMARY

1. The yield from the reaction of nitrogen dioxide with benzene is found to increase proportionally with the dilution of the hydrocarbon. Saturation of the mixture with oxygen strongly accelerates the reaction.

2. From the reaction products were isolated nitrobenzene, m- and p-dinitrobenzenes, symm.-trinitrobenzene, 2,4-dinitrophenol, 2,4,6-trinitrophenol, and oxalic acid.

3. It is shown that dinitro- and trinitrobenzenes are formed when the reaction is performed in sealed tubes at 100-150° with high dilution of the nitrogen dioxide with benzene, and also at the ordinary pressure and temperature.

4. The previously advanced theory of the interaction of nitrogen dioxide with aromatic hydrocarbons is developed. According to this, the primary stage of the reaction in a nonpolar medium is the intermediate formation of the product of addition of the electrophilic and radical-like molecule of NO_2 to the benzene ring. Transformations of the resultant radical under nitration conditions lead to the observed reaction products.

5. In conformity with the theory it is found that the main component of the mixture of nitrocresols resulting from the reaction of nitrogen dioxide with toluene is trinitro-m-cresol, while with chlorobenzene the main product is trinitro-m-chlorophenol.

LITERATURE CITED

[1] A.I. Titov, J. Gen. Chem., 17, 382 (1947); 18, 192 (1948); 19, 517 (1949). *

[2] H. Wieland, Ber., 54, 1776 (1921).

[3] J. Meisenheimer, Ann. 330, 147 (1904).

[4] J. Schmidt, Ber., 33, 3251 (1900).

[5] A. I. Titov, J. Gen. Chem. 18, 465, 473, 534 (1948).

[6] N. Puranen, Chem. Zentr., II, 856 (1933).

[7] A. I. Titov, J. Gen. Chem. 18, 741 (1948).

Received June 26, 1948
Resubmitted August 1, 1951

* See Consultants Bureau translation, p. 467.

THE MECHANISM OF NITRATION OF AROMATIC COMPOUNDS WITH NITRIC ACID

III. NITRATION OF BENZENE WITH DILUTE NITRIC ACID

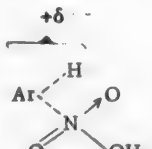
A. I. Titov and A. N. Baryshnikova

In our previous communications [1,2] it was shown that the nitration of aromatic compounds with nitric acid up to a certain concentration of the latter (characteristic for each compound) proceeds through intermediate interaction with nitrogen dioxide. In these cases the nitric acid merely serves as a source of nitrogen dioxide and as a medium for its regeneration from lower oxides. The strength of the nitric acid required for development of the catalytic action of nitrogen dioxide upon nitration is very high (> 80%) for highly nucleophilic aromatic substances such as naphthalene and phenolic ethers. Preliminary experiments have shown that in the nitration with nitric acid of benzene itself and of compounds with still lower reactivity, the accelerating effect of nitrogen dioxide is only manifested at relatively low concentrations of the order of 20-30% and lower. The theory of these phenomena has been considered in the previous communications [1,2].

On the other hand we have found [3] that during the action of nitrogen dioxide on benzene at temperatures of 100° and higher, even at very high dilution with the hydrocarbon, the reaction product consists of approximately equal amounts of symm.-trinitrobenzene, picric acid and nitrobenzene. These data led us to the conclusion that the principal products of reaction of dilute nitric acid with benzene must be polynitro derivatives — trinitrobenzene and picric acid. Experiment has fully confirmed this paradoxical conclusion. Trinitrobenzene was formed also when nitration was carried out with more concentrated nitric acid in presence of nitrogen dioxide, but in these cases its formation was accompanied to a greater or lesser degree by "normal" nitration of benzene, leading exclusively to nitrobenzene and minute amounts of nitrophenols. In conformity with our theory the minimization of normal nitration was promoted by addition of nitrates. The mechanism of interaction of benzene with oxides of nitrogen has been considered in our recent paper [3], and the theory of "normal" nitration has also been recently discussed [2], the latter in more detail in another paper [4]. In a general form the results of the present investigation have already been published [5].

The causes of the extreme difficulty of nitration of the aromatic nucleus with molecules of nitric acid have been previously discussed. The following ideas are put forward to supplement our earlier explanations. The molecule of nitric acid, and still more the nitrate ion:

is conspicuously stable thanks to the conjugation of the π- and p-orbitals, interaction of the orbitals necessitating parallelism between the axes of the respective electrons, for otherwise the atoms of nitrogen and oxygen would be arranged in the same plane. In the development of the transition complex (A):



(A)

the arrangement of the atoms around the nitrogen will deviate from the planar distribution and will approach the tetrahedral arrangement; this will upset the conjugation and lead to an increased activation energy. These hindrances, likewise steric hindrances, are absent during formation of the transition complexes of Ar—H with the nitronium cation NO_2^+, with the nitrosyl cation NO^+, and with the monomer of nitrogen dioxide NO_2, which also favors their formation.

The above considerations may also be applied to the understanding of the characteristics of certain other reactions.

EXPERIMENTAL

1. Nitration of benzene with dilute nitric acid in sealed tubes. Nitration was performed in two sealed tubes, capacity about 100 ml. In each of these was charged 20 ml benzene, 20 ml nitric acid, specific gravity 1.1, 10 g potassium nitrate and 0.2 g trioxymethylene (the latter to speed up formation of oxides of nitrogen). Heating at 135° was continued for 10 hours. The contents of the tubes were combined and treated first with water and then with soda solution. Acidification of the soda extract gave 0.52 g picric acid, m.p. 117-120° (no depression in mixed melting point test). Distillation of the organic layer by heating to 135° at the ordinary pressure brought over benzene. Distillation was then continued in vacuum (12 mm) when 0.62 g nitrobenzene came over. The residue (0.48 g) in the distillation flask crystallized and gave a positive reaction with dilute alkali for symm.-trinitrobenzene. After a single recrystallization from alcohol the product melted at 118° and did not depress the melting point of an authentic specimen of symm.-trinitrobenzene.

2. Nitration at normal pressure. 100 ml nitric acid (specific gravity 1.32), 1 l benzene and 2 g trioxymethylene were heated in a flask under a reflux condenser for 50 hours at a bath temperature of 60-65°. The acid layer was then separated and replaced by a fresh portion of nitric acid and trioxymethylene prior to continued heating for another 50 hours. The benzene layer was worked up as in the preceding experiment with water and soda solution. From the soda extract was obtained 1.6 g pure picric acid. The benzene was driven off from the organic layer under a low vacuum; then at about 80° and a pressure of 6 mm, nitrobenzene (12 g) came over. The residue of 2.41 g in the distillation flask was steam-distilled. The oily distillate (0.6 g) was not further examined; the residue (1.5 g)partly crystallized and gave a definite reaction for symm.-trinitrobenzene. Recrystallization from alcohol yielded 0.7 g trinitrobenzene with m.p. about 118° (no depression in the mixed melting point test).

3. Demonstration of formation of symm.-trinitrobenzene on nitration of benzene with nitric acid through the intermediate interaction of the hydrocarbon with nitrogen dioxide. a) For the heterogeneous reaction. Into each of two tubes was charged 2 ml benzene and 40 ml nitric acid (s.g. 1.1). To one of the tubes was added 8 g ammonium nitrate to destroy any nitrogen dioxide that might form. To the other tube was added 10 g potassium nitrate together with 0.05 g trioxymethylene for promoting nitrogen dioxide formation. Both of the tubes were heated for 4 hours at 120°. In the first tube, i.e. the one in which nitrogen dioxide could not be formed, the benzene was entirely unchanged and could be distilled off on the water bath. In the case of the second tube, using the previously described method, separation was effected of 0.07 g trinitrobenzene and 0.05 g picric acid.

Similar experiments using nitric acid of s.g. 1.2 gave (in absence of nitrogen dioxide) 0.12 g nitrobenzene and (in presence of nitrogen dioxide) 0.15 g trinitrobenzene, 0.1 g picric acid and about 0.1 g nitrobenzene. Experiments with nitric acid of s.g. 1.3 gave (in absence of nitrogen dioxide) 1.77 g nitrobenzene and (in presence of nitrogen dioxide) 1.7 g nitrobenzene, 0.15 g trinitrobenzene and 0.2 g picric acid.

b) For the homogeneous reaction. Into each of two tubes was charged 2 ml benzene, 15 ml glacial acetic acid and 5 ml nitric acid, s.g. 1.4. To the first tube was added 0.5 ammonium nitrate to destroy any nitrogen dioxide that might be formed, and to the second tube was added 0.1 g trioxymethylene to promote nitrogen dioxide formation. From the reaction mass of the first tube (i.e. in the absence of nitrogen dioxide) was obtained 1.02 g nitrobenzene and traces of nitrophenols. From the second tube, in which the reaction proceeded in presence of nitrogen dioxide, were separated 0.8 g nitrobenzene, 0.12 g crystalline symm.-trinitrobenzene and 0.17 g picric acid.

SUMMARY

In conformity with the previously developed theory it was found that the nitration of benzene with dilute nitric acid of s.g. below 1.2 proceeds substantially only through intermediate interaction with nitrogen dioxide and leads to the formation of a mixture of approximately equal parts of symm.-trinitrobenzene, picric acid and nitrobenzene. Increasing concentrations of nitric acid leads to an increase in the content of nitrobenzene, formed with participation of nitrogen dioxide, in the reaction product.

LITERATURE CITED

[1] J. Gen. Chem., 17, 382 (1947).
[2] J. Gen. Chem. 19, 517 (1949); see Consultants Bureau translation, p. 467.
[3] J. Gen. Chem. 22, 1329 (1952). see Consultants Bureau translation, p. 1373.
[4] J. Gen. Chem. 18, 733 (1948).
[5] J. Gen. Chem. 18, 192 (1948).

Received June 26, 1948. Resubmitted August 1, 1951.

THE BEHAVIOR OF KETONES TOWARDS AMMONIACAL SILVER OXIDE SOLUTION

V. I. Veksler

In the scientific literature and in textbooks is firmly entrenched the statement that an ammoniacal solution of silver oxide is a specific reagent for aldehydes which permits aldehydes to be differentiated from ketones (the silver mirror test [1]). In Liebig's handbook [2] it is stated that the reagent is prepared by adding to the aldehyde under test a small amount of ammonia and a solution of silver nitrate. Tollens [3] points out that the addition of excess ammonia sharply diminishes the sensitivity of the reagent described by Liebig. With the aim of eliminating this danger and also of increasing the sensitivity, he recommends the addition of caustic alkali to the reagent. Addition of alkali has also been recommended for the purpose of oxidizing aldehydes [4]. It must be pointed out that many authors have referred to the silver mirror reaction without being clear as to whether or not alkali is present.

In the literature we have only found one reference to an α,β-unsaturated ketone (3-methylcyclohexene-2-one-1) capable of giving the silver mirror reaction [5]. The reaction is also given by aliphatic diketones [6]. No indications of the ability of saturated monoketones to react with ammoniacal silver oxide solution have been found in the literature. However, as our investigations have shown, some ketones react with extraordinary ease with the ammoniacal silver oxide solution prepared by Tollens' method (with addition of caustic alkali). Examples are methylbenzyl ketone, dibenzyl ketone, p-tolylacetone, and unsymm. diphenylacetone. On addition of the reagent to the ketone in the cold, the solution at once darkens, black metallic silver is later precipitated, and a brilliant metallic mirror is formed on the walls of the vessel. The course of the reaction is particularly clear in the case of methylbenzyl ketone, p-tolylacetone and dibenzyl ketone. Unsymm. diphenylacetone reacts much more slowly. The reaction velocity is at a maximum during the first two hours, after which it rapidly slows down, coming practically to a standstill after 48-72 hours.

The data presented below for the behavior of ketones towards ammoniacal silver oxide solution were obtained predominantly with methylbenzyl ketone. We established that the reagent prepared from silver nitrate and ammonia in the absence of alkali does not act upon ketones in the cold (various ratios were tested, ranging from 2.3 to 10 moles NH_3 per mole $AgNO_3$). Addition of alkali in the equivalent amount (in relation to the silver) leads to an intense reaction. The excess of alkali acts as an accelerator. A large excess of ammonia hinders the reaction (see Table 1). Thus the inhibiting action of excess ammonia on the oxidation of aldehydes by silver oxide, as described in the literature [3], is also characteristic of the present reaction. The inhibiting effect is also reported in the literature in relation to oxidation of monohydric alcohols, oxycarbonyl compounds and oxyacids [7,8,11].

We also investigated the action of the reagent prepared by solution in ammonia of freshly precipitated and washed silver oxide. It was revealed that this reagent intensively oxidizes the ketones mentioned even without addition of caustic alkali. This may be explained by the obstinate retention by the precipitated silver oxide of part of the precipitating agent (alkali) [12]. The amount of silver oxide actually participating in the reaction (over a period of 48-72 hours) when using a solution with a given concentration of silver, alkali and ammonia was found to depend also on the relative amounts of starting substances: the higher the ratio of silver oxide to ketone the larger the amount entering into reaction. Thus, for the case investigated, when the initial ratio of Ag_2O to ketone was raised from 0.23 to 3.42, the consumption of silver oxide increased from 0.22 to 0.65 mole per mole of initial ketone (Table 2).

Examination of the products of reaction of ketones with the silver reagent did not reveal the presence of carboxylic acids which are the characteristic end products of conversion of aldehydes under similar conditions. Apart from metallic silver the reaction products contain resinous substances of a neutral character. Methylbenzyl ketone yielded a liquid resin with a yellow color which hardened slowly in the air, but rapidly in presence of acid. Similar products were obtained from the other ketones. Colloidal solutions containing an organic resin and metallic silver in the form of a stable sol were sometimes formed in experiments using a low concentration of alkali and also high dilutions.

At present it is impossible to explain the mechanism of the above reaction. The ability of ketones to react with ammoniacal silver oxide solution must be intimately bound up with the characteristic structures of ketones. The ketones investigated are characterized by the general structure $ArCH_2COR$ or Ar_2CHCOR, where Ar is an aromatic radical. All these ketones contain the $-CH_2-$ (or $>CH-$) group arranged between an aromatic group and carbonyl, and the carbonyl group is located in the β-position to the aromatic radical. Ketones lacking this characteristic structure are incapable of entering into reaction with ammoniacal silver oxide solution. We have thus found that the following do not react under the described conditions: Methyl hexyl ketone, which does not contain an aromatic radical; benzylacetone, in which the carbonyl group is separated from the phenyl radical by two CH_2 groups; propiophenone, in which the carbonyl group directly adjoins the aromatic nucleus. It is impossible to assert that the ability of ketones to enter into the reaction is associated with enolization, since ethylacetoacetate does not react with the silver reagent under the specified conditions.

Ketones of the general formula $ArCH_2COR$ or Ar_2CHCOR are distinguished by the presence of a reactive hydrogen in the CH_2 and CH groups, due to the influence of the carbonyl group and the aromatic radical. This feature actually distinguishes them from the series of investigated ketones incapable of reacting with the silver reagent, and evidently this characteristic determines the course of the reaction.

It may be suggested that silver oxide first oxidizes the CH_2 or CH group and that the resultant oxidation products then condense with formation of resins. It is possible, however, that condensation of the ketone takes place under the influence of the alkali in presence of the complex silver ions, and the resultant condensation products undergo oxidation (followed by condensation). Either of these mechanisms will be facilitated by the presence of an active CH_2 or CH group.

We carried out blank experiments to clarify the action of aqueous solutions of alkali and ammonia (in the absence of silver) on methylbenzyl ketone. It was found that on prolonged standing (several weeks) the ketone is converted into a liquid resin which gradually hardens in the air. The aqueous layer then gives the silver mirror reaction on addition of an ammoniacal silver oxide solution, although it no longer contains ketone. The absence of the latter is confirmed by the failure of the organic substance extracted from the aqueous layer to react with semicarbazide. These facts support the second mechanism which assumes that the first step is condensation, followed by oxidation. It must be admitted, however, that in experiments on the oxidation of the ketone with the silver reagent, the starting ketone was identified in the reaction mixture after the lapse of 24 hours in spite of the presence of unconsumed silver oxide. Consequently it is impossible to assert that the ketone at first entirely undergoes condensation, and therefore the results of the blank experiments cannot be regarded as evidence of the mechanism of the reaction.

EXPERIMENTAL

Investigated ketones. Methylbenzyl ketone, synthesized according to [9], b.p. 110-115° (25 mm), $n_\alpha^{20.5}$ 1.51168, $n_\beta^{20.5}$ 1.52857, semicarbazone m.p. 181-183°; p-tolylacetone synthesized according to [10], b.p. 117-118° (16 mm); dibenzyl ketone was purified via the semicarbazone, m.p. 33°; diphenylacetone, m.p. 61°; benzylacetone, prepared by hydrogenation of benzalacetone, b.p. 230-232°. In the control experiments freshly distilled ketones were used.

To a weighed amount of ketone in a flask of ordinary glass was added the oxidizing reagent, the flask was shaken several times by hand and then left to stand at room temperature. The progress of the reaction was followed by titration of samples with 0.01 N KCNS solution.

1) A silver oxide precipitate was obtained by the action of potassium hydroxide on silver acetate in the cold; it was filtered, washed with water, dissolved in ammonia (silver concentration $2.23 \cdot 10^{-5}$ g-equiv/ml; ammonia concentration $1.1 \cdot 10^{-4}$ mole/ml). To 1 g methylbenzyl ketone was added 300 ml of the ammoniacal solution. The solution became noticeably darker after a few minutes and a silver mirror was subsequently formed. The silver content of the solution after 24, 72, and 144 hours was respectively 0.46, 0.31, and $0.29 \cdot 10^{-5}$ g-equiv./ml (temperature 13-16°).

2) The oxidizing solution was prepared by adding sodium hydroxide and ammonia to a silver nitrate solution (silver concentration $2.25 \cdot 10^{-5}$; ammonia concentration $2 \cdot 10^{-4}$; concentration of excess alkali $2.3 \cdot 10^{-5}$ g equiv/ml). 250 ml of the solution was run into 1.5 g methylbenzyl ketone. After 24 hours the silver content of the solution was $0.35 \cdot 10^{-5}$ g-equiv/ml. The aqueous solution was run through a filter, the precipitate on the

filter and at the bottom of the flask (mirror) was washed with alcohol and then carefully washed several times with ether. After evaporation of the solvents in vacuum, the alcohol-ether extract gave 0.8 g of viscous resin with a light-yellow color. The resin gradually hardened when kept in a desiccator over calcium chloride. The aqueous layer was extracted with ether; evaporation of the ether left 0.3 g oil which formed a semicarbazone with m.p. 179-180°; the melting point of the mixture with the semicarbazone of the original ketone was 179-181°. The precipitate on the filter and at the bottom of the flask (metallic silver) dissolved completely in 50% HNO_3.

3) The oxidizing solution was prepared from equivalent amounts of $AgNO_3$ and NaOH with addition of ammonia until the Ag_2O precipitate dissolved. 200 ml of the solution was added to 0.5 g methylbenzyl ketone. After 72 hours the silver concentration had fallen from 3.3 to $0.8 \cdot 10^{-5}$ g-equiv/ml. The aqueous solution was poured through a filter, the precipitate on the filter and at the bottom of the flask was repeatedly treated with ether. The ether extract was evaporated in vacuum, leaving a viscous resin with a pleasant fresh odor.

With the aim of checking the ketone content of the resin, it was treated with alcohol when it partially dissolved. Semicarbazide solution was added to the alcoholic extract; a resin was precipitated which was completely soluble in ether; no semicarbazone was obtained.

After evaporating the ethereal solution of the resin in a vacuum desiccator over sulfuric acid, the residue had a yellow-orange color and could be readily ground to a powder. This had a faint odor. It softened and melted gradually over the range of 92-120°.

When the resin from which the ethereal extract had been made had been kept over sulfuric acid in a vacuum desiccator for several days, it was converted into a fine red powder with a faint odor, melting gradually between 62-75°.

0.0885 g substance: 0.2638 g CO_2. 0.0851 g substance: 0.2532 g CO_2; 0.0500 g H_2O. Found %: C 81.3, 81.2; H 6.6. $C_9H_{10}O$. Calculated %: C 80.6; H 7.05.

4) Mixtures were prepared from silver oxide and silver nitrate with various proportions of alkali and ammonia. To the mixtures were added weighed amounts of methylbenzyl ketone. After 72 hours samples were titrated. Some data illustrating the results obtained are presented in Table 1.

TABLE 1

CONSUMPTION OF SILVER OXIDE FOR OXIDATION OF METHYLBENZYL KETONE AS A FUNCTION OF THE INITIAL CONCENTRATION OF ALKALI AND AMMONIA (after 72 hours)

No.	Weight of ketone		Vol. of solution (ml)	Concentration of initial reagents (g-equiv/ml)				Consumption of silver (g-equiv · $\cdot 10^5$)	Molar ratio of consumed Ag_2O to initial ketone
				Silver ($\cdot 10^5$)		NaOH	NH_3 ($\cdot 10^4$)		
	g	mole · $\cdot 10^4$		Taken in form of Ag_2O	Taken in form of $AgNO_3$				
1	0.057	4.26	20	2.48	–	–	1.5	34.8	0.41
2	1.0	75	300	2.23	–	–	1.1	585	0.39
3	0.057	4.26	20	2.48	–	$5 \cdot 10^{-6}$	1.5	36.4	0.43
4	0.057	4.26	20	2.48	–	$5 \cdot 10^{-4}$	1.5	49.2	0.53
5	0.057	4.26	20	–	1.83	–	0.9	0	0
6	0.057	4.26	20	–	1.90	$4.5 \cdot 10^{-7}$	1.3	0	0
7	0.057	4.26	20	–	1.83	$5 \cdot 10^{-6}$	0.9	8.4	0.1
8	0.057	4.26	20	–	1.83	$5 \cdot 10^{-5}$	0.9	35.6	0.42
9	0.057	4.26	20	–	1.83	$5 \cdot 10^{-4}$	0.9	36.6	0.43
10	0.057	4.26	23	–	1.82	$4.4 \cdot 10^{-5}$	43.5	0	0

A sample of experiment 10 was placed in a vacuum desiccator in the cold under a residual pressure of 25 mm. With progressive loss of ammonia the reaction (darkening and a silver precipitation) became more and more intense.

5) Weighed amounts of methylbenzyl ketone were taken in the approximate ratios of 1:2:4:8:16.* To each was added 25 ml alkaline ammoniacal silver oxide solution (silver concentration $2.25 \cdot 10^{-5}$; ammonia concentration $2.0 \cdot 10^{-4}$; excess alkali as calculated $2.3 \cdot 10^{-5}$ g-equiv./ml). After 96 hours the silver concentration was determined and the consumption of Ag_2O per mole of ketone was calculated. Data showing the relation between silver oxide consumption and the initial ratio of reagents are presented in Table 2.

* Publisher's note. The ratios are actually those of Ag_2O to ketone (see third column of Table 2).

TABLE 2

DEPENDENCE OF THE CONSUMPTION OF SILVER OXIDE ON THE RATIO OF SILVER OXIDE TO KETONE

Weight of ketone		Initial molar ratio Ag_2O: ketone	Final silver concentration (g-equiv/ml · 10^5)	Molar ratio of Ag_2O consumed to initial ketone
g	mole			
0.1630	$1.2 \cdot 10^{-3}$	0.23	0.09	0.22
0.0975	$0.73 \cdot 10^{-3}$	0.38	0.67	0.27
0.0450	$0.43 \cdot 10^{-3}$	0.83	0.25	0.37
0.0220	$1.6 \cdot 10^{-4}$	1.71	1.48	0.58
0.0110	$0.82 \cdot 10^{-4}$	3.42	1.83	0.64

6) 0.05 g methylbenzyl ketone was allowed to stand with 140 ml of 2.5% solution of NaOH. After 18 days a liquid resin (0.25 g) with a yellow color had formed at the bottom. Part of filtrate (90 ml) was extracted several times with ethyl acetate. After driving off the solvent there remained 0.1 g of liquid which did not react with semicarbazide. To the remaining 50 ml of filtrate was added 10 ml of ammoniacal (alkaline) silver oxide solution (silver concentration $3 \cdot 10^{-5}$ g-equiv/ml). Darkening immediately developed. By the next morning there was no silver in solution, and at the bottom was a precipitate of metallic silver, also an organic substance. Consequently the aqueous layer contains a substance which does not react with semicarbazide but is susceptible to oxidation by ammoniacal silver oxide solution.

SUMMARY

It is shown that a series of alkaryl ketones of the general formula $ArCH_2COCH_3$ or $Ar_2CHCOCH_3$ reacts in the cold with alkaline ammoniacal silver oxide solution to form a silver mirror. In the light of these data the alkaline ammoniacal silver oxide solution is not a specific reagent for differentiating aldehydes from ketones.

LITERATURE CITED

[1] For example, P. Shorygin, Course of Organic Chemistry, 173 (1940).

[2] J. Liebig, Handb. org. Chem., 135 (1843).

[3] B. Tollens, Ber., 14, 1950 (1881); 15, 1635, 1828 (1882).

[4] Houben, Methods of Organic Chemistry, Vol. II, part 1, 59 (1941); Einhorn, Ber., 26, 454 (1893).

[5] A. Bluman and O. Zeitschel, Ber., 46, 1178 (1913).

[6] L. Loquin, Bull.Soc.chim., (3), 31, 1173 (1904)

[7] D. R. Maxted, J. Chem. Soc., 1926, 2178.

[8] K. Dreyer, . Ann., 416, 203 (1918).

[9] Organic Syntheses, I, 313 (1949).

[10] T.I. Temnikova and V.I. Veksler, J. Gen. Chem., 19, 1318 (1949). •

[11] V. Ivanov and K. Sokova, Proc. Acad. Sci., U.S.S.R., 63, 279 (1948).

[12] G Remi, Textbook of Inorganic Chemistry, Vol. 2, 226 (1935).

Received February 1, 1951

• See Consultants Bureau translation, p. 1315.

THE ACTION OF ETHYL CHLOROCARBONATE UPON ORGANOMAGNESIUM COMPOUNDS

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The reaction between organometallic compounds and esters of haloacids was first studied by A. M. Butlerov [1]. He obtained the following reaction on treating methyl zinc with ethyl chlorocarbonate: $2ClCOOC_2H_5 + Zn(CH_3)_2 = 2CO_2 + 2C_2H_4 + 2CH_4 + ZnCl_2$. On reacting methyl zinc with methyl chlorocarbonate Butlerov obtained: CO_2, CH_3Cl and C_2H_4. In 1903 a paper appeared by A.N. Reformatsky [2] on the synthesis of tertiary alcohols by the action of allyl iodide and zinc on esters of halo acids in ethereal solution, when he obtained alcohols with three olefinic bonds. He proposed a reaction mechanism. Later authors [3] worked with esters of halo-substituted acids and halogenated organomagnesium compounds. Later still Iotsich [4] obtained triallylene carbinol and Matsurevich [5] triethyl carbinol and tripropyl carbinol.

The aim of our investigation was the further study of this reaction and the preparation with its help of substances about which little has been published. Our researches indicate the applicability of this reaction not only to the preparation of tertiary alcohols but also to the preparation of esters. For the preparation of the former a large excess of the organomagnesium compound is taken and is added to the chlorcarbonic ester, while for the preparation of esters the starting products are taken in equal amounts, the chlorocarbonic ester being added to the formed organomagnesium compound. The reaction proceeds according to the scheme put forward by A.N. Reformatsky. It can likewise proceed according to Houben's scheme.

EXPERIMENTAL

1. Synthesis of triallylcarbinol. Allyl magnesium bromide was prepared in a three-necked round-bottomed flask fitted with a mercury seal, a mechanical stirrer, a reflux condenser and a dropping funnel. Its yield was checked by titration of a sample with 0.1 N sulfuric acid using methyl orange as indicator. Through one of the necks of the flask was inserted a siphon, and a second opening served for withdrawal of samples. During the reaction the latter opening was closed. For the performance of the second stage of the reaction, i.e. the reaction with ethyl chlorocarbonate, the ethereal solution of allyl magnesium bromide was siphoned under pressure of dry hydrogen into another flask likewise equipped with mechanical stirrer, reflux condenser and dropping funnel. A special device was inserted in the siphon for trapping the fine magnesium turnings. In the course of stirring over a period of two hours addition was made to the ether solution of the complex of the calculated amount of freshly distilled ethyl chlorocarbonate dissolved in three times the volume of absolute ether. With progressive addition of the ethyl chlorocarbonate the temperature of the liquid rose and it became lighter in color. The reaction was completed by heating on a hot water bath. The end of the reaction was checked by the color reaction of Gilman and Schultze [6]. The contents of the flask were then decomposed with ice and sulfuric acid, and the ether layer was separated from the aqueous layer. The latter was twice extracted with ether and the extracts added to the main layer. The combined ether layer was washed with 10% sodium carbonate solution and after separation it was dried with calcium chloride. The ether was distilled off, leaving in the flask a yellowish liquid boiling at 189-192°. This was a mobile liquid with a faint yellow color and a terpene-like odor, insoluble in water, readily soluble in alcohol and ether. It does not oxidize in the air. After keeping for about a year the preparation had scarcely changed in boiling point. Its constants and analysis are detailed in Table 1. It gave a positive reaction for teriary alcohols in the Deniges test [7]. The phenylurethane melts at 239°. All the analyses confirm the preparation of triallylcarbinol.

This carbinol was prepared for the first time by A.N. Reformatsky [8] by the action of zinc on 1 mole ethyl chlorocarbonate and 3 moles allyl iodide in ether solution. The experiment lasted 3 months. Reformatsky attempted to conduct the reaction in presence of metallic magnesium (in place of zinc), but it proceeded rather stormily with much heat development even with good cooling and slow addition of the ethereal solution of the mixture of allyl

TABLE 1

Triallyl carbinol	B. p.	d_4^{21}	n_D^{21}	MR_D	Parachor*	Found % C	Found % H	Reaction with C_6H_5NCO	% OH*	Duration of expt.	Yield (in %)
Our preparation	189-192°	0.8791	1.468	47.8933	391.2	78.41 79.31	10.62 10.82	Reacts	10.88	10-12 hours	66.66
Reformatsky's preparation [8]	191-192°	0.8781	1.468	47.8933	–	78.64 78.52	10.76 10.63	–	–	3 mos.	27.50

* $C_{19}H_{16}O$. Calculated: MR_D 48.15; P 404.5; %: C 78.94. H 10.52; OH 10.17.

TABLE 2

Tri-n-butylcarbinol	B. p.	d_4^{15}	n_D^{15}	MR_D*	Parachor*	Found % C	Found % H	Reaction with C_6H_5NCO	% OH*	Yield (in %)
Our preparation	129-132° at 20 mm	0.8332	1.4370	62.338	550.4	77.65 77.94	13.74 14.38	Reacts	8.2	81.25
Ivanov's preparation [10]	120 at 10 mm	d_4^{18} 0.8440	n_D^{18} 1.4448	–	–	–	–	Does not react	–	51.00

* $C_{13}H_{28}O$. Calculated MR_D 63.76; P 554.59; %: C 78.00; H 14.00; OH 8.5.

iodide and haloester to the magnesium. This variant was therefore considered unsuitable for the preparation of unsaturated compounds. Reformatsky's method also involved large losses of allyl iodide by evaporation over the long period of the reaction.

2. Synthesis of tri-n-butyl carbinol. Butyl magnesium bromide prepared in the above-described apparatus by the usual method was transferred to the other flask. Ethyl chlorocarbonate was introduced over a period of 2 hours. Heat was evolved also in this reaction. The reactionproduct was decomposed and worked up as in Experiment 1. Following the distillation of the ether the flask contained a syrupy, light-yellow liquid. Fractionation yielded a fraction boiling at 129-132° (20 mm). Its constants and analysis are detailed in Table 2. The phenylurethane formed light-yellow crystals, m.p. 147.5°. Deniges' reagent gave a negative result.

Tri-n-butylcarbinol was obtained by Moyer and Marvel [9] from butyl magnesium bromide and ethyl carbonate in 84% yield. B. p. 129-131° (20 mm). Some data are reported by Ivanov [10] who obtained the alcohol from butyl magnesium bromide and CO_2.

3. Synthesis of triisoamylcarbinol. Isoamyl magnesium bromide was prepared by the usual method. The procedure for the second stage of the synthesis was the same as above. After removal of the ether the flask contained a colorless, viscous liquid which was distilled under reduced pressure. Fractionation yielded a fraction with b. p. 136-140° (at 10 mm), soluble in alcohol and ether. Yield 88% of the theoretical. Negative reaction in the Deniges test. d_4^{20} 0.8362; n_D^{20} 1.443; MR_D 75.088; calculated 77.61; σ 30.61.

Parachor. Found: P 680.6; calculated 671.5. Found %: C 79.39; H 14.10; OH 6.63. $C_{16}H_{34}O$. Calculated %: C 79.30; H 14.05; OH 7.02. The phenylurethane melted at 147.8°.

Triisoamylcarbinol was first prepared by Grignard [11] from carbonyl chloride and isoamyl magnesium bromide with b. p. 140° (10 mm). There are no other data in the literature.

4. Synthesis of ethyl propionate. The prepared ethyl magnesium bromide was charged into a flask containing the equivalent amount of ethyl chlorocarbonate. Fractionation of the reaction product gave a fraction (yield 50%) boiling at 99-105°; d_4^{20} 0.9547; n_D^{20} 1.333; MR_D 26.709; calculated 26.944. Analysis of the silver salt of propionic acid following hydrolysis of the ester: Ag 61.02%; Calculated 59.64%. Only the following constants appear in the literature [12] for ethyl propionate: b. p. 98-99°; d_4^{20} 0.8907.

5. Synthesis of ethyl valerate. The method of preparation was the same as in the preceding experiment.

Fractionation gave a fraction (yield 26%) boiling at 32-40° (10 mm); d_4^{20} 0.8828; n_D^{20} 1.412; MR_D 36.18. The prepared ester was hydrolyzed. The silver salt of valeric acid gave (%): Ag 50.29; calculated: 51.64. In the literature the following constants are reported for ethyl valerate [13]: b.p. 144.4° (at 736.5 mm); d^{20} 0.8765.

6. Synthesis of ethyl isocaproate. Preparation was by the same method as in the previous experiment. Yield 28% of the theoretical. A fraction boiling at 50-53° (10 mm) was isolated; d_4^{20} 0.8700; n_D^{20} 1.405; MR_D 39.72; calculated 40.11. The ester was hydrolyzed and the silver salt of isocaproic acid was obtained. Found (%): Ag 47.97; calculated 48.38. The constants given in the literature [14] for ethyl isocaproate are: b.p. 160.4° (737 mm); d^{20} 0.8705.

SUMMARY

1. In a series of experiments it was established that tertiary alcohols (both saturated and unsaturated) and esters are obtained by the reaction of ethyl chloro-carbonate with organomagnesium compounds.

2. Tri-n-butylcarbinol and triisoamylcarbinol (about which there is little information in the literature) were prepared and investigated.

3. The method of preparation of triallylcarbinol has certain advantages over Reformatsky's method, namely: Reduction in the duration of the reaction from 3 months to 10-12 hours and a considerable decrease in the loss of starting materials.

4. The Deniges reaction is not characteristic for all tertiary alcohols. In particular it gives negative results with tri-n-butylcarbinol and triisoamycarbinol.

LITERATURE CITED

[1] A. N. Reformatsky, Monohydric Unsaturated Alcohols of the Aliphatic Series. Moscow, 354 (1908).

[2] A. N. Reformatsky, J. Russ. Chem., Soc., 35, 1017 (1903).

[3] L. Henry, Chem.Zentr., II, 15 (1906).

[4] Zh. I. Iotsich, J. Russ. Chem. Soc., 42, 1495 (1910).

[5] I.K. Matsurevich, J. Russ. Chem. Soc., 42, 1582 (1910); Chem.Zentr., I, 1500 (1911).

[6] Henry, Gilman, and F. Schulze, Chem.Zentr., II, 1781 (1925).

[7] Deniges, Comptes rend., 126, 1043, 1277 (1898).

[8] A. N. Reformatsky. Chem.Zentr.,I, 736 (1909).

[9] W. W. Moyer and C. S. Marvel, Chem.Zentr., I, 2984 (1931).

[10] D. Ivanov, Chem.Zentr.,I, 2072 (1925).

[11] W. Grignard, Comptes rend., 136, 815 (1903); Chem.Zentr., I, 1077, (1903); Beilst., I, 430.

[12] Beilst., II, 240.

[13] Beilst., II, 301.

[14] Beilst., II, 328.

Received July 14, 1950

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BIS-TRICHLOROPHOSPHAZOSULFONE

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For the purpose of investigating the trichlorophosphazosulfone grouping (I) it would be interesting to have a compound in which the properties of the trichlorophosphazosulfone group were not obscured by those of any other combined groups.

At the present time two types of phosphazosulfone compounds are known: Trichlorophosphazosulfone aryls (II) [1] and the anhydride of trichlorophosphazosulfuric acid chloride (III) [2]. In the first type the trichlorophosphazosulfone group is combined with various aryl radicals, in the secondtype with chlorine. Consequently in the trichlorophosphazosulfone aryls the properties of the aryl radicals are superposed on those of the trichlorophosphazo group, and the anhydride of trichlorphosphazosulfuric acid is both a trichlorophosphazosulfone compound and the anhydride of a chlorosulfonic acid.

A compound with a "pure" trichlorophosphazosulfone group not bound to any "foreign" groups is bistrichlorophosphazosulfone (IV) which is undoubtedly the best model for a study of the properties of the trichlorophosphazosulfone group. Compound (IV) has so far be en unknown. The objective of the present investigation was its preparation.

$-SO_2-N{=}PCl_3$ (I); $ArSO_2N{=}PCl_3$ (II); $ClSO_2N{=}PCl_3$ (III); $Cl_3P{=}NSO_2N{=}PCl_3$ (IV).

For the purpose of preparation of bistrichlorophosphazosulfone the same route was selected as for the preparation of other trichlorophosphazosulfone compounds [1,2], i.e., the action of phosphorus pentachloride on the appropriate sulfamide, in this case the simplest sulfamide, according to the equation:

$$2PCl_5 + NH_2SO_2NH_2 \rightarrow 4HCl + Cl_3P{=}NSO_2N{=}PCl_3.$$

It transpired that the reaction proceeds very readily in this direction, even at room temperature, and is accompanied by development of heat. At 100° the reaction proceeds violently and is completed in a few minutes. It is more convenient to perform the reaction at first at 50-60° and to raise the temperature to 100° only towards the end. If the selected reactants are chemically pure substances in exactly stoichiometric proportions, or, better, with a slight excess of phosphorous pentachloride, then the quantity of hydrogen chloride separated and the amount of bistrichlorophosphazosulfone formed are respectively within 1.0 and 0.3% of the theoretical amounts.

As first prepared, bistrichlorophosphazosulfone is a colorless liquid resembling glycerol in viscosity and appearance. After two weeks one of the specimens had crystallized to a lustrous, perfectly dry and very hard mass melting at 40.5 (maximum from 39°) - 41.5° (the latter with the thermometer bulb immersed in the liquid). The melted substance very easily supercools, and in the absence of seeds it can be kept in liquid form at room temperature for many days. The substance is readily soluble in benzene, toluene, ether and acetone; difficultly soluble in petroleum ether. Bistrichlorophosphazosulfone does not fume in the air but very quickly deliquesces. Fine crystals of the compound react quietly with water. When larger crystals (0.2-0.3g) are introduced into water, the substance at first spreads out and then rapidly dissolves with evolution of heat and with a characteristic noise. Large amounts react with water instantaneously and very violently. If a small quantity of bistrichlorophosphazosulfone is placed on a wet filter paper, a violent reaction starts within a few seconds, the paper chars, and a strong odor of burnt sugar is developed. Bistrichlorophosphazosulfone vigorously reacts with aqueous and anhydrous ammonia, amines, alcohols, phenols, and organometallic compounds. In a vacuum of 0.5 mm it does not distill undecomposed.

Bistrichlorophosphazosulfone is very difficult to recrystallize because of its exceptional ease of solution in the majority of organic solvents; from a mixture of solvents with petroleum ether it separates as an oily layer.

About 50 g of substance separates from a solution of 110.0 g bistrichlorophosphazosulfone in 5.0 ml benzene at 20°. Consequently, at 20° about 60 g bistrichlorophosphazosulfone is dissolved in 5.0 ml benzene. The bistrichlorophosphazosulfone obtained by recrystallization from benzene is in the form of large, colorless, transparent platelets with a length of up to 8 mm. It will be well understood that all possible precautions against access of moisture from the air must be applied to the substance and its solution. Fortunately, the preparation of chemically pure bistrichlorophosphazosulfone does not necessitate recrystallization, for the perfectly pure substance can be

easily obtained directly from the reaction without any special purification, but this calls for the use of perfectly pure starting materials and thorough removal of the excess of phosphorus pentachloride by heating in vacuum.

EXPERIMENTAL

Quantitative experiment. Into a round-bottomed two-necked 100 ml flask were introduced 0.21 mole pure phosphorus pentachloride (43.74 g) and 0.1 mole pure sulfamide (9.61 g) which had been thoroughly dried in vacuum. A cork was at once attached in which was inserted a reflux condenser with a broad tube serving as a receiver for the excess phosphorus pentachloride, and a narrow tube for escape of the hydrogen chloride. A slow stream of dry air was passed through the second tube throughout the whole period of the experiment. The top end of the reflux condenser was connected to two absorbers containing 0.6 equivalents of potassium hydroxide dissolved in 900 g water. The flask was rotated and shaken to facilitate mixing of the sulfamide with the phosphorus pentachloride. Hydrogen chloride at once begins to come off, as indicated by the "currents" in the first absorber. Through the reflux condenser is passed iced water in order to retain the phosphorus pentachloride as well as possible, and the flask is immersed in a water bath heated to 60°. Evolution of hydrogen chloride is intensified; after a few minutes the reaction mixture begins to liquefy and after 6-7 minutes it has the appearance of a semiliquid gruel. After 20 minutes the bath temperature is raised to 90° and after 30 minutes the reaction is at an end. The reaction mass is a colorless, transparent liquid in which float a few particles of excess phosphorus pentachloride. In the reflux condenser and on the cold parts of the flask is deposited a thin layer of phosphorus pentachloride. The stream of dry air is passed through for a further 15 minutes, after which the contents of the absorbers are mixed and made up with water to a weight of 1000 g.

Neutralization of 25.00 g of the solution required 24.52 ml 0.2 N acid. Found: 0.4038 equivalent of hydrogen chloride. Calculated (from the reaction equation): 0.4000 equivalent.

The amount of hydrogen chloride found is thus 0.95% more than the calculated amount. The probable explanation of this is that the phosphorus pentachloride was not fully condensed in the condenser tube and was partly entrained by the stream of hydrogen chloride and dry air. In order to remove the excess of phosphorus pentachloride, the tube through which air was blown was closed, the upper end of the condenser was connected to a vacuum and the flask was heated on a boiling water bath so that the entire surface of the flask was heated by steam. If this is not done, part of the phosphorus pentachloride is deposited in the neck of the flask. The phosphorus pentachloride is completely removed in the course of one hour at a vacuum of 6-8 mm and at the temperature of the boiling water bath. Bistrichlorophosphazosulfone remains in the flask in the form of a transparent, colorless liquid which at once crystallizes after cooling and seeding. Weight of product 36.81 g or 100.3% of the theoretical amount calculated on the sulfamide. M.p. 39.7-41.0. After heating in a 2 mm vacuum at 130° for 15 minutes, the melting point rose to 40.5-41.5°. Addition of a little dry benzene to the melted substance followed by cooling caused the bistrichlorophosphazosulfone to crystallize in the form of large, dense transparent platelets with the same melting point (see general part).

Preparation of bistrichlorophosphazosulfone. Into a round-bottomed half-liter flask are introduced 0.3 mole dry sulfamide (28.83 g) and 0.63 mole pure phosphorus pentachloride (131.24 g). The flask is closed with a cork through which passes a broad reflux condenser whose upper end is connected to a downwardly sloping glass tube 20-30 cm in length and 3-4 mm in diameter. This tube takes the place of a calcium chloride tube. The reaction mixture is well stirred by rotating the flask which is then placed on a water bath heated to 60-70°. The reaction proceeds as in the quantitative experiment. At the end of the reaction the upper end of the reflux condenser is connected to a vacuum and the total surface of the flask is heated, first for one hour on the boiling water bath and then for 15-30 minutes on an oil bath at 130°. Starting from perfectly pure substances, the yield of bistrichlorophosphazosulfone is about 100% of theory and the m. p. is 40.5-41.5°. If technical phosphorus pentachloride has been used the melting point is depressed by several degrees. Care should be taken that there is a slight excess of phosphorus pentachloride. When working with technical phosphorus pentachloride it must be remembered that it contains a fairly large proportion of phosphorus oxychloride so that it might easily happen that there is an excess of sulfamide. If there is a slight excess of sulfamide the melting point of the product is lowered by 3-4° and a large proportion of the sulfamide rapidly crystallizes from the liquid bistrichlorophosphazosulfone in the form of transparent thin platelets. For complete removal of the sulfamide the product must be dissolved in three times the volume of dry benzene, the sulfamide sucked off, and the benzene driven off in vacuum; however, it is best so to conduct the reaction that an excess of phosphorus pentachloride is present. For the properties of bistrichlorophosphazosulfone see the general part.

Analyses of bistrichlorophosphazosulfone. Analyses were performed on the substance with m.p. 40.5-41.5°, prepared from chemically pure materials. The molecular weight was determined by the cryoscopic method in benzene solution. Nitrogen, sulfur, phosphorus and chlorine were determined by the usual methods after hydrolysis of the weighed sample of bistrichlorophosphazosulfone in aqueous solution. The acids were titrated after hydrolysis, using thymolphthalein as indicator.

0.2114 g, 0.2367 g substance: 0.3723 g, 0.4162 g AgCl. 0.4979 g, 0.4857 g substance; 0.3158 g, 0.3095 g $BaSO_4$. 0.5891 g, 0.5426 g substance: 0.3560 g, 0.3274 g $Mg_2P_2O_7$. 0.7068 g, 0.7886 g substance: 19.35 ml, 21.62 ml 0.2 N Acid. 0.1184 g, 0.1079 g substance: 19.41 ml, 17.68 ml 0.2 N alkali. 0.1591 g, 0.3291 g substance; 20.0 g benzene: Δt 0.112°, 0.235°. Found %: Cl 57.88, 57.80; S 8.71, 8.75; P 16.82, 16.79; N 7.67, 7.68. Equivalents of acid on hydrolysis: 12.03, 12.02; M 360.1, 355.0. $Cl_6SP_2N_2O_2$. Calculated %: Cl 57.99; S 8.74; P 16.89; N 7.68. Equivalents of acid on hydrolysis: 12.00; M 366.8.

SUMMARY

Bistrichlorophosphazosulfone has been prepared and some of its properties described.

LITERATURE CITED

[1] A. V. Kirsanov, J. Gen. Chem., 21 . 81 (1951); see Consultants Bureau translation, p. 93.

[2] A. V. Kirsanov, J. Gen. Chem., 21 88 (1951); see Consultants Bureau translation, p. 101.

Received December 23, 1950

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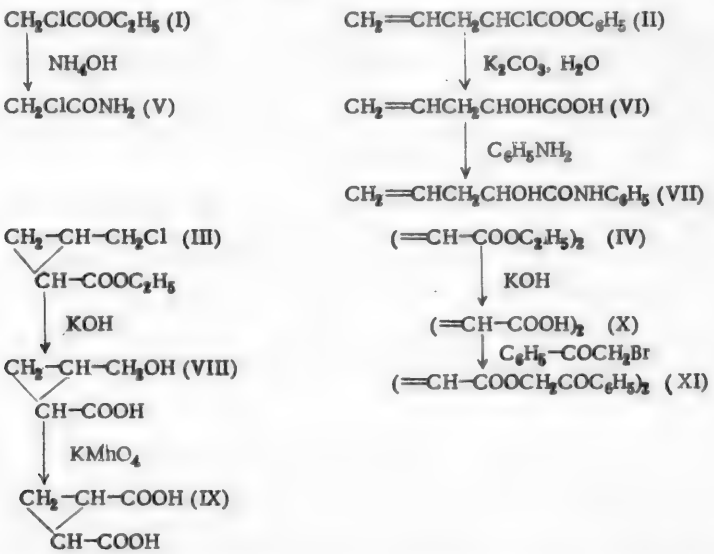
REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

XI. THE REACTION OF ETHYL DIAZOACETATE WITH ALLYL CHLORIDE

I. A. Dyakonov and N. B. Vinogradova

In one of the previous communications [1] of this series it was shown that reaction of ethyl diazoacetate with allyl bromide gives a 70% yield of the ethyl ester of α-bromallylacetic acid. The purpose of the present study is the examination of the reaction of ethyl diazoacetate with allyl chloride. The investigation has shown that in analogy with the allyl bromide reaction, the ethyl ester of α-chlorallylacetic acid is formed (II), but this is not the sole reaction product. By careful fractionation of the crude condensation product it was possible to isolate, in addition to the ester (II), the esters (I) and (III), while evidence was obtained of the presence of an ester (IV) in the fractions boiling higher than ester (III) (see experimental part).



The above reaction scheme also illustrates the further course of the investigation which was undertaken with the aim of establishing the structure of the compounds obtained. Compounds (II), (III), and (VII) are here described for the first time. Compounds (VI), (VIII) and (X) were not isolated in the analytically pure form in the course of this investigation. The first substance which we succeeded in isolating by fractionation of the crude reaction product was ethyl chloroacetate (I). This was identified by conversion into chloracetamide (V). The formation of ethyl chloroacetate during the reaction of ethyl diazoacetate with allyl chloride confirms the observations of Buchner [2] concerning the ability of ethyl diazoacetate to remove hydrogen halide from esters of halo-substituted acids. • It may be assumed that in our case the cleavage of hydrogen halide proceeded from ester (II) and not from ester (III) since the latter route is hardly probable [13]. However, the possibility is not excluded of direct cleavage of hydrogen halide from the allyl chloride which is present in the reaction mixture in large excess. No experimental confirmation of this possibility has yet been found.

• A fresh examination of the product of reaction of ethyl diazoacetate with allyl bromide showed that, in addition to the ester of α-bromallylacetic acid, a small amount of ethyl bromoacetate is also formed (see experimental part).

The second substance isolated during fractionation of the crude product was the ethyl ester of α-chlorallylacetic acid (II). It was hydrolyzed with potassium carbonate solution to give α-hydroxylallylacetic acid which we were unable to isolate in the perfectly pure form due to the small amount obtained. The acid was characterized by conversion to the anilide (VII) whose identity was confirmed by a melting point test in admixture with an authentic specimen and by determination of the nitrogen content.

The data obtained permit us to ascribe the formula (II) to the investigated chloride. Concerning the mechanism of formation of this chloride we may put forward the same two suggestions that were advanced when discussing the mechanism of formation of the ethyl ester of α-bromallylacetic acid [1].

In view of the fact that among the products of reaction of ethyl diazoacetate with allyl chloride was found the ester of 2-chloromethylcyclopropane-1-carboxylic acid(III) (see below), we took the opportunity of examining its susceptibility to isomerization into the unsaturated chloride (II) under conditions similar to those of its formation. The control experiment performed for this purpose gave a negative result: Prolonged heating of the investigated chloride with excess of allyl chloride in presence of cuprous chloride as catalyst did not reveal any influence on the starting chloride. The indicates that the cyclic chloride (III) cannot be an intermediate product in the synthesis of the unsaturated chloride (II) in the reaction here investigated.

The cyclic chloride (III) was the third substance isolated during fractionation of the crude reaction product. The chloride contained a trace of ethyl fumarate which we were able to eliminate by treatment with cold permanganate solution.

In order to establish the structure of the chloride (III) it was hydrolyzed by alkali to the cyclic hydroxy acid (VIII) which could not be separated in the pure form due to the small amount available. Evidence that the acid resulting from the hydrolysis really was trans-2-(hydroxymethyl)-cyclopropane-1-carboxylic acid was obtained by oxidizing it with potassium permanganate to trans-1,2-cyclopropane dicarboxylic acid which is well known in the literature. On this evidence it would also be permissible to claim that the structure of chloride (III) has been elucidated.

On the basis of the data presented in the experimental part it may be suggested that the fractions obtained by further fractionation of the crude reaction product and boiling higher than chloride (III) are a mixture of this chloride with ethyl fumarate.* Alkaline hydrolysis of these fractions led to formation of fumaric acid, characterized in the form of its diphenacyl ester.

Consideration of the results of reaction of ethyl diazoacetate with allyl bromide on the one hand, and of those with allyl chloride on the other, indicate that the activity of the C—Hal bond in allyl bromide is greater than that in allyl chloride. **

EXPERIMENTAL

Condensation of allyl chloride with ethyl diazoacetate. Into a round-bottomed flask fitted with a stirrer, dropping funnel and reflux condenser was introduced 600 g freshly distilled allyl chloride and 2.4 g cuprous chloride.*** The mixture was heated on the water bath while being mechanically stirred; after reaching the boiling point, slow addition was made from the dropping funnel (without stopping the heating) of 188.8 g ethyl diazoacetate mixed with an equal volume of allyl chloride. The evolved gas passed through a trap immersed in a freezing mixture and was collected in a gasholder. The total volume of evolved nitrogen was 33.52 l (15° and 767 mm) or 85% of theory.

The experiments showed that during the reaction the catalyst (cuprous chloride) underwent a partial change (color change to bright orange) and part went into solution to form a complex compound with allyl chloride.

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* In view of the fact that the boiling point of the investigated fractions is considerably above the boiling point of ethyl fumarate, it is possible that they are admixed with the product of the condensation of ethyl diazoacetate with the ester of the α-chlorallylacetic acid.

** Comparative evaluation of the relative activity of the halogen in allyl chloride, bromide and iodide was made by Tronov and Gershevich [3] who found that the activity ratio was 1:860:4300 (in reaction with pyridine) and 1:85:138 (in reaction with sodium methylate).

*** The condensation reaction was performed in presence of the following catalysts: Copper bronze (Natur cupfer C.) and cuprous chloride. It was found that the reaction does not proceed in presence of copper sulfate; with the other two catalysts equally good results are obtained (compare [1]).

These compounds were removed at the start of the reaction by filtering off the reaction mixture from the catalyst, washing with dilute hydrochloric acid (1:1) and then washing with sodium carbonate solution. In order to avoid loss of substance during these washing treatments, the wash liquors were extracted with ether, and the residues from the ether extracts (after removal of solvent) were added to the main bulk. The reaction mixture was then dried with calcium chloride and freed from excess allyl chloride by heating on the water bath. The remaining material, a dark-colored liquid, was distilled in a 10 mm vacuum without separation into fractions. In the distillation flask remained a large amount of thick, dark-colored resin. The distillate came over in a wide temperature range (from 40 to 110°) at 10 mm.

The resultant complex mixture of products was subjected to fractionation in a vacuum column with a dephlegmator at 10 mm. Even after repeated fractionation it was impossible to separate the constituents completely, but three main components were isolated, incidentally, in almost analytical purity (see introduction). The results of fractionation are shown in the table.

RESULTS OF FRACTIONATION OF CONDENSATION PRODUCTS

No. of fraction	B. pt.	Weight (in g)	Name of substance in fraction
1	40-41°	16.7	Ethyl chloroacetate
2	42-66	9.0	Intermediate fraction
3	66-67	16	Ethyl ester of α-chlorallylacetic acid
4	67-83	16.1	Intermediate fraction
5	83-87	11.9	Ethyl ester of 2-(chloromethyl)-cyclopropane-1-carboxylic acid
6	87-92	14.8	Ethyl fumarate in admixture with the cyclic chloride and with other chlorides
7	92-96	8.0	
8	96-100	6.0	
9	100-110	12.6	

Ethyl chloroacetate. (I). This was isolated in the analytically pure form by direct fractionation in a vacuum column (Table 1). B. pt. 40-41° (10 mm); 142-143° (760 mm); d_4^{20} 1.1406; n_D^{20} 1 4202; MR_D 27.20; calculated 27.19.

Found %: Cl 28.77, 28.81. M 123.3, 119.9. $C_4H_7O_2Cl$. Calculated %: Cl 28.96. M 122.56.

Literature data: B. pt. 142.6-143° at 750 mm [4]; 52° at 20 mm [5]; d_4^{20} 1.1520; n_D^{20} 1.4216 [4].

Chloracetamide (V). 2 ml of the substance under investigation was shaken in a test tube with 2 volumes of 20% ammonia at 0°. The crystals of chloracetamide obtained after recrystallization from alcohol melted at 119-120° (no melting point depression in admixture with an authentic specimen).

Ethyl ester of α-chlorallylacetic acid (II). Like the chloride (I) it was separated in analytical purity by direct fractionation of the crude reaction product. B. pt. 66-67° (10 mm); d_4^{20} 1.0530; n_D^{20} 1.4400; MR_D 40.72; calculated 40.58.

0.1673 g substance: 0.1472 g AgCl. 0.2458 g substance; 17.1 g benzene: Δt 0.46°. 0.4171 g substance: 17.1 g benzene: Δt 0.78°. Found %: Cl 21.77; M 160.0, 160.4. $C_7H_{11}O_2Cl$. Calculated %: Cl 21.86; M 162.62.

Hydrolysis of the ester (II). Into a round-bottomed flask fitted with a stirrer and a mercury seal was introduced 14 g of the substance under examination and 119 g 10% potassium carbonate solution. Boiling and mechanical stirring of the reaction mixture were continued up to disappearance of the layer of oily ester (about 2 hours). The cooled solution was acidified with sulfuric acid (Congo red indicator) and extracted with ether. After drying the ether extract and distilling off the ether, there remained 3.3 g of viscous, dark-colored oil which we assumed to be α-hydroxyallylacetic acid.* The liquid did not, however, crystallize either on standing in a vacuum desiccator over sulfuric acid or on cooling to −10°. For the purpose of identification the acid was converted into the anilide by the method of Shriner and Fuson [6]. The crystals of anilide had a yellow color and were decolorized by boiling with animal charcoal. After recrystallization from alcohol the m. pt. was 77-78°.

0.1244 g substance: 7.8 ml N_2 (20°, 775.2 mm) 0.2042 g substance: 13.2 ml N_2 (19°, 772.7 mm). Found %: N 7.38, 7.61. $C_{11}H_{13}O_2N$. Calculated %: N 7.33

By a similar method we obtained the anilide of authentic α-hydroxyallylacetic acid. A mixture of both of the anilides did not exhibit any melting point depression.

Ethyl ester of 2-(chloromethyl)-cyclopropane-1-carboxylic acid (III). Fraction 5, Table 1 (crude chloride).

* We were the first to prepare this acid by hydrolysis of the ethyl ester of α-bromallylacetic acid. It formed very hygroscopic crystals melting at 37° [1].

B. pt. 83-87° (10 mm); n_D^{20} 1.4530.

0.1686 g substance: 0.1402 g AgCl. 0.2363 g substance: 0.1951 g AgCl. Found %: Cl 20.56, 20.42. $C_7H_{11}O_2Cl$. Calculated %: Cl 21.82.

In order to remove the admixed ethyl fumarate, 30.4 g of the crude chloride (III) was shaken in the cold with potassium permanganate until the violet color of the permanganate ion had disappeared; this required 17.0 g permanganate. After filtration, the manganese dioxide was washed with ether and the filtrate in turn was extracted with ether. The ether extracts were combined and dried, the ether distilled off, and the flask residue fractionated to give 21.1 g of a chloride with the following constants:

B. pt. 82-84° (8 mm); d_4^{20} 1.1091; n_D^{20} 1.4560; MR_D 39.87; calculated 38.87. Found: Increment for a three-membered ring 1.0.

0.1284 g substance: 0.1120 g AgCl. 0.2538 g substance: 0.2248 g AgCl. 0.1948 g substance; 17.32 g benzene: Δt 0.37°, 0.2673 g substance; 17.03 g benzene: Δt 0.52°. Found %: Cl 21.58, 21.89; M 156.0, 154.9. $C_7H_{11}O_2Cl$. Calculated %: Cl 21.86; M 162.62.

Hydrolysis of chloride (III). Into a flask with a reflux condenser were introduced 14.8 g cyclic chloride and 11.6 g potassium hydroxide dissolved in methyl alcohol. The reaction mixture was heated on the water bath for one hour. The precipitate of potassium chloride was filtered off, the excess alkali neutralized with carbon dioxide, the methyl alcohol removed by boiling with water on the water bath, and the residue after acidification was extracted with ether.

Removal of the ether left 8.1 g of syrupy liquid which we took to be 2-(hydroxymethyl)-cyclopropane-1-carboxylic acid (VIII). Part of the acid was used for preparation of the silver salt:

Found %: Ag 46.2. $C_5H_8O_3$. $C_5H_7O_3Ag$. Calculated %: Ag 48.54.

The low content of silver found in the silver salt indicates that the acid was impure.

Oxidation of the hydroxy acid (VIII). Oxidation of 3.9 g of acid (VIII) was effected by shaking its aqueous solution with an excess (2 g) over the calculated (7 g) amount of potassium permanganate. This required, in all, two days. The excess permanganate was destroyed with a few drops of bisulfate, the manganese dioxide filtered off, the solution was concentrated on the water bath, acidified with sulfuric acid and extracted with ether. From the ether extract was isolated 1.26 g (28.97% of theory) of a colorless, crystalline acid with a m.pt. 165°. After two crystallizations from water the m. pt. was constant at 172°.

Found %: C 46.51; H 5.04; equiv. 65.40. $C_5H_6O_4$. Calculated %: C 46.17; H 4.65; equiv. 65.05.

No melting point depression occurred when mixed with an authentic specimen of trans-cyclopropane-1,2-dicarboxylic acid prepared by one of us by another route [7].*

Investigation of the isomerizing tendency of the cyclic chloride (III). 8.9 g of chloride (III), 70 g allyl chloride and 0.2 g cuprous chloride were heated to boiling on the water bath with mechanical stirring for three hours. The catalyst was filtered off from the cooled solution and the filtrate well washed, first with dilute hydrochloric acid and then with soda solution as detailed above. The solution was then dried with calcium chloride, the excess allyl chloride was distilled off, and the residue distilled in vacuum. The constants of the distillate did not differ from those of the original chloride (III), so that we may conclude that chloride (III) is not susceptible to isomerization under the conditions of the investigated reaction.

Ethyl fumarate (IV). The percentage content of halogen was determined in fractions 7, 8 and 9 (see table) as, respectively, 15.30, 7.37 and 5.90. All three fractions were unsaturated in the permanganate test. Fraction 7 (7.7 g) was heated on the water bath for 30 minutes with a solution of 7.8 g potassium hydroxide in methyl alcohol. The precipitate of potassium chloride was filtered off; the filtrate, diluted with water, was evaporated on the water bath to drive off the methyl alcohol and then acidified with sulfuric acid prior to ether extraction. Removal of the ether left an oil of honey-like appearance. On adding to it a mixture of ether and petroleum ether, a crystalline acid, m. pt. 276°, separated out. In view of the fact that fumaric acid melts with decomposition so that the literature data on its melting point vary widely, we converted the acid into its diphenacyl ester [9], m. pt. 197°. In admixture with an authentic specimen melting at 197.5° [10], the melting point was not depressed. On this evidence we can assume the presence of ethyl fumarate in fraction 7.

* In the literature [8] the m. pt. of trans-cyclopropane dicarboxylic acid is given as 175°.

Reaction of ethyl diazoacetate with allyl bromide*. Condensation of 79.05 g ethyl diazoacetate with excess allyl bromide (450 g) in presence of 0.5 g copper powder, followed by vacuum fractionation of the reaction product at 12 mm, gave two fractions: 1) 69-78°, 15.15 g; 2) 78-79°, 114 g.

As we have previously shown [1], fraction (2) is the ethyl ester of α-bromallylacetic acid. Examination of fraction (1) revealed the possibility of separating from it, by repeated fractionation at normal pressure, about 2 g of substance with high lachrymatory power, b. pt. 158-162°, at 760 mm; n_D^{16} 1.453.

Found %: Br 46.98. $C_4H_7O_2Br$. Calculated %: Br 47.84. Literature cited: b. pt. 158.2 at 760 mm [11], n_D^{13} 1.454 [12].

On the basis of the above constants and of the analytical data we may assume that the isolated bromide was not completely pure ethyl bromoacetate (this ester is known to be a strong lachrymator).

SUMMARY

1. It is shown that the reaction of ethyl diazoacetate with allyl chloride in presence of copper catalysts yields the ethyl esters of the following acids: chloracetic, α-chlorallylacetic, 2-(chlormethyl)-cyclopropane-1-carboxylic, and fumaric.

2. The structures were established of the esters (unknown in the literature) of α-chlorallylacetic and 2-(chlormethyl)-cyclopropane-1-carboxylic acids. The anilide of α-chlorallylacetic acid was prepared.

3. It is shown that the ester of 2-(chlormethyl)-cyclopropane-1-carboxylic acid does not isomerize to the ester of α-chlorallylacetic acid when heated with excess allyl chloride in presence of cuprous chloride.

4. In a further study of the ethyl diazoacetate-allyl bromide condensation, it was found that ethyl bromacetate is formed to a very slight extent.

LITERATURE CITED

[1] Dyakonov and Vinogradova, J. Gen. Chem., 21, 851 (1951).**

[2] Buckner, Papendick, . Ann., 273, 222 (1898).

[3] Tronov and Gershevich, J. Russ. Phys. Chem. Soc., 59, 727 (1927).

[4] Beilstein, Vol. II, p. 88.

[5] Forster, Newman, J. Chem. Soc., 97, 2573 (1910).

[6] Shriner and Fuson, Systematic Qualitative Analysis of Organic Compounds, p. 162 (1950).

[7] Dyakonov and Pirogova, J. Gen. Chem., 21, 1979 (1950).***

[8] Guthzeit, Lobeck, J.prak.Chem., [2] 77, 53 (1906).

[9] Johnson, Shennan and Reed, Organic Reagents for Organic Analysis, p. 85 (1948).

[10] Rathner, Reid, J. Am. Chem. Soc., 41, 80 (1919).

[11] Beilstein.

[12] Perkin. J. Chem. Soc., 65, 427 (1894).

[13] Dyakonov, J. Gen. Chem., 10, 402, 414 (1940); 15, 473 (1945).

Received January 31, 1951

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* See also [1]

** See Consultants Bureau translation, p. 933.

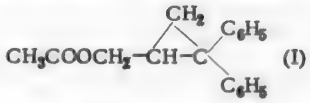
*** See Consultants Bureau translation, p. 2201.

REACTIONS OF ALIPHATIC DIAZO COMPOUNDS WITH UNSATURATED COMPOUNDS

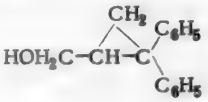
XII. CONDENSATION REACTIONS OF DIPHENYLDIAZOMETHANE AND ETHYL DIAZOACETATE WITH ALLYL ACETATE

I. A. Dyakonov and O. V. Guseva

Following up the papers by one of us on the reactions of ethyl diazoacetate [1] and diphenyldiazomethane [2] with allyl alcohol, we report here on the reaction of the same diazo compounds with allyl acetate. Diphenyldiazomethane readily reacts with boiling allyl acetate and, in contrast to the reaction with allyl alcohol, it forms one main reaction product: 1-(acetoxymethyl)-2,2-diphenylcyclopropane (I), which is a new compound.



(I)



(II)

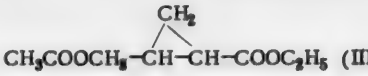
The assignment of the acetate (I) to the cyclopropane series was confirmed by its conversion into the cyclic alcohol (II), previously prepared by one of us [2] from diphenyldiazomethane and allyl alcohol. The identity with the authentic specimen was established by comparison of their physical constants and by the determination of the mixed melting point of their 3,5-dinitrobenzoates. The yield of the analytically pure preparation of the acetate (I) was 55.25% of the theoretical yield. The chief losses of yield arise during vacuum rectification of the crude reaction product (the latter contains benzophenone which is not easily separated from the compound (V) by distillation. In the pure form benzophenone was only isolated in a yield of 3.5% of theory.* In place of the nearly colorless ketazine, there were separated from the crude condensation product two sorts of crystals with a yellow color: with m. pt. 157-158° and m. pt. 172-173°, the former predominating. Since the analytical data (nitrogen content, molecular weight) point to the crystals melting at 157-158° being the ketazine $C_{26}H_{20}ON_2$, and the melting point of a mixture with authentic ketazine [4] (m. pt. 162°) was not depressed, we are entitled to assume that the crystals in question are actually ketazine but contaminated with a substance of apparently similar composition. With the aim of determining the composition of this impurity, the crystals were hydrolyzed with 20-30 % sulfuric acid when three hydrolysis products were obtained: Benzophenone, hydrazine sulfate and tetraphenylethane. According to Curtius (4) hydrolysis of authentic ketazine under the same conditions only gave two products – benzophenone and hydrazine sulfate:

$$(C_6H_5)_2C = N-N = C(C_6H_5)_2 \xrightarrow[H_2SO_4]{2H_2O} (C_6H_5)_2C = O + H_2N-NH_2 \cdot H_2SO_4.$$

From the nitrogen content and the molecular weight, the crystals melting at 172-173° also correspond to $C_{26}H_{20}ON_2$, but the mixture with ketazine had the depressed melting point of 154-155°, and hydrolysis with sulfuric acid gave, in addition to benzophenone and hydrazine sulfate, twice as much tetraphenylethane as the same weight of crystals with m. p. 157-158°. The data suggest that the substance melting at 172-173° is actually the impurity in ketazine which caused the melting point to be depressed to 157-158° and which gave rise to tetraphenylethane among the hydrolysis products. The lack of material at our disposal prevented us from establishing the structure of this impurity which was isolated in the form of crystals with m. pt. 172-173°.

The reaction of ethyl diazoacetate with allyl acetate was performed, as customary, in presence of copper catalysts (anhydrous copper sulfate, copper bronze). The yield of the principal product of this reaction – the ethyl ester of 2-(acetoxymethyl)-cyclopropane-1-carboxylic acid – is 70.6% of the theoretical yield, but the crude

* According to Staudinger and co-workers [3] benzophenone is a very minor product of the decomposition of diphenyldiazomethane.



(III)

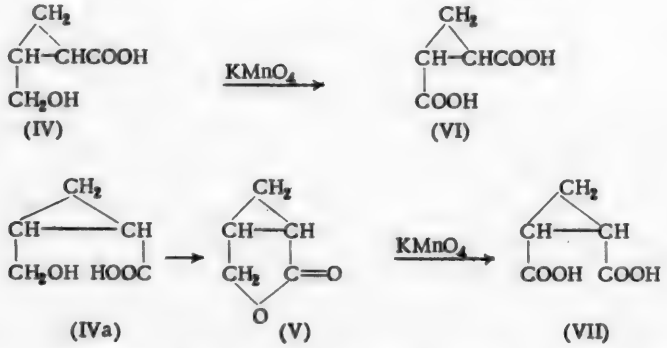
preparation contains a small admixture of ethyl fumarate which could not be completely removed by fractional distillation.

The ester (III) (yield 62.7% of theory calculated on the ethyl diazoacetate) was obtained in the perfectly pure form after treatment of the crude ester with cold potassium permanganate solution. Among the oxidation products was oxalic acid, which by analogy with previous investigations in this field was assumed to be proof of the formation of ethyl fumarate. A rough calculation based on the consumption of oxidizing agent shows that the ethyl fumarate content of the crude ester (III) does not exceed 3% of the weight of (III). The constants of the crude preparation likewise only differ slightly from those of the purified ether (III).

Measurement of the Raman spectra* of the ester (III) (see experimental part) confirmed the presence of the cyclopropane nucleus. In accordance with the literature data on this subject (for literature see Comm. VII of this series) the frequencies 862 (2), 1202 (3) are characteristic of the disubstituted cyclopropane ring. For the carbonyl group of the ester (III) the frequency 1729 (3) was found. Alkaline hydrolysis of ester (III) gave the corresponding 2-hydroxymethylcyclopropane-1-carboxylic acid (IV) in the form of a mixture of crystals and oily liquid. The yield of crude acid (IV) is 80% of theory based on the original ester (III). The crystalline acid proved to be the trans-isomer of the cyclic hydroxy acid (IV), since oxidation with potassium permanganate gave the well-known trans-cyclopropane-1,2-dicarboxylic acid (VI) in 84.6% yield. Our further research revealed that the oily acid was a mixture of trans- and cis-hydroxymethylcyclopropane carboxylic acids. Careful vacuum distillation of this mixture resulted in cleavage of water from the cis-acid (IVa) with formation of a bicyclic lactone (V) which we have isolated and characterized. The trans-isomer of the acid (IV) was obtained by crystallization of the undistilled residue.

The lactone ring of (V) is easily opened under the action of caustic alkali solutions and is converted by permanganate oxidation into cis-cyclopropane-1,2-dicarboxylic acid (60% yield). These reactions determine its structure. In addition, measurements of the Raman spectra** are in harmony with the formula (V). The presence of the trimethylene ring is indicated by the frequencies 850 (9), 1171 (7), 2981 (4), 3002 (5) and 3085 (8).*** A conspicuous feature is the displacement into the long-wave region of the spectrum of the first two of the above-mentioned lines, which must undoubtedly be ascribed to the influence of conjugation with the cyclopropane 5-membered ring. To the latter corresponds the frequency 899 (4). The frequency of the carbonyl group of the lactone (1760 cm^{-1}) slightly exceeds the frequency of the carbonyl group in other compounds (1730 cm^{-1}).

On the basis of the amount of lactone (V) obtained, the yield of cis-isomer of the acid (IVa) in the hydrolysis reaction is only 7% of the theoretical. The yield of trans-isomer (IV) is 55.7% of the theoretical. We may assume that the corresponding stereoisomeric forms of ester (III) will also occur in the same ratio (1:8).



(IV) (VI) (IVa) (V) (VII)

Of the compounds described above, three have been prepared for the first time: the cyclic ester (III), the trans-isomer of the hydroxy acid (IV) and the bicyclic lactone (V).

EXPERIMENTAL

I. Condensation of diphenyldiazomethane with allyl acetate. Starting materials were: a) Allyl acetate prepared by the method of Swanson and Coss [6]. B. pt. 103-104.5°; d_4^{17} 0.9277; n_D^{17} 1.4047. (Literature data:

* Measurements were performed by A.P.Ryskalchuk to whom the authors convey their thanks.

** All measurements and calculations were performed by M.E.Shmulyakovsky to whom we express our deep gratitude.

*** The remaining frequencies are enumerated in the experimental part.

b. pt. 103.5-104°; d_4^{18} 0.9279; n_D^{18} 1.4048. No active hydrogen was found, indicating absence of allyl alcohol (b. pt. 97°). b) Diphenyldiazomethane was prepared as in [5].

Synthesis. Into a reaction flask fitted with a reflux condenser and a dropping funnel was introduced 75 ml allyl acetate, and in the dropping funnel was placed 33-38 g diphenyldiazomethane mixed with the same volume of allyl acetate. The diphenyldiazomethane is slowly added dropwise to the boiling allyl acetate.

The reaction is accompanied by evolution of nitrogen and change of color of the solution. Towards the end of the experiment the color of the solution changes from dark-red (the color of diphenyldiazomethane) to light yellow. In the manner described, separate portions of diphenyldiazomethane, totalling in all 216.6 g, were reacted. At the end of the reaction the solutions from the individual experiments were combined and the excess allyl acetate distilled off in a 150 mm vacuum. The residue in the distillation flask was diluted with cold ethyl alcohol; at this point it was noted that deep-colored crystals first separated with an m.pt. of 165-170° (2.2 g). Further dilution of the reaction product with ethyl alcohol (up to 10-12 times the volume) led to crystallization of not so deeply colored crystals. The total amount of the latter was 12.5 g. M. pt. 152-155°. After several recrystallizations from alcohol and from alcohol-benzene mixture, the first portion of cyrstals melted at 172-173°; the second portion, after recrystallization from the same solvents, had the raised m. pt. of 157-158°. See below for further details of the examination of the crystals with m.pt. 172-173° and 157-158°.

The alcoholic mother liquor from the crystals, containing in solution the main reaction product, was subjected to distillation in vacuum at 25-30 mm to drive off the alcohol, and the residue (a dark, viscous oil) was fractionated in vacuum (0.5 mm). As the result of a series of repeated fractional distillations, the condensation product which had first come over in a wide temperature range was separated into the following fractions (at 0.5 mm): First fraction 107-120°, n_D^{16} 1.594, 8 g; second fraction, 120-135°, n_D^{16} 1.591, 6 g; third fraction, 135-150°, n_D^{16} 1.578-1.568, 15 g; fourth fraction, 147-150°, n_D^{16} 1.564, 163.7 g.

On the basis of further studies, the fourth (main) fraction was taken to be the cyclic acetate (I); the first and second fractions were considered to be a mixture of benzophenone and the acetate (I); the third fraction was apparently an intermediate one; it was resolved by further distillation into a series of separate subfractions whose refractive indices varied within the above-stated limits. The yield of pure acetate (I) was 163.7 g or 55.25% of the theoretical

The most sensitive measure of the purity of acetate (I) proved to be the refractive index and not the boiling point. The entire distillation process was therefore checked by the value of n_D of the individual fractions. For the fourth fraction or acetate (I) a constant n_D was obtained which did not change after the second distillation. In the case of the remaining fractions it was impossible to attain a constant n_D due to the smallness of the quantities.

II. 1-(Acetoxymethyl)-2,2-diphenylcyclopropane (I). The freshly distilled preparation was a fairly viscous, light-yellow oil; the viscosity was higher than that of the corresponding alcohol (II). It turns a deeper yellow in storage while the refractive index increases slightly. B. pt. 165-167° (2 mm); 147-150° (0.5 mm); $d_4^{20.5}$ 1.0914; n_D^{20} 1.5620; MR_D 79.12; calculated 78.28. Exaltation 0.84.

0.1409 g substance: 0.4180 g CO_2; 0.892 g H_2O. 0.3176 g, 0.3181 g substance; 16.01 g, 16.64 g benzene: Δt 0.37, 0.37°. Found %: C 80.93; H 7.08; M 275.1, 264.3. $C_{18}H_{18}O_2$. Calculated %: C 81.19; H 6.84; M 266.3.

Hydrolysis of acetate (I). A mixture of 17 g potassium hydroxide dissolved in 90 ml methyl alcohol with 52.5 g acetate (I) was heated for 1½ hours on the water bath under a reflux condenser. The excess alkali was neutralized with carbon dioxide, the potassium carbonate was filtered off, and the methyl alcohol distilled off in vacuum. The flask residue was dissolved in ether and the ethereal solution was washed with water and dried with calcium chloride. The very viscous yellow oil remaining after removal of the solvent was distilled in vacuum: B. pt. 165-167° (3.5 mm); n_D^{51} 1.583. The 3,5-dinitrobenzoate melted at 140° and did not depress the m. pt. of the 3,5-dinitrobenzoate of the cyclic alcohol (II) (m. pt. 140°) described by one of us [2]. Yield of alcohol (II) in the hydrolysis reaction was 37.0-38.8 g or 83.8-87.8% of the theoretical.

III. Investigation of the by-products of the reaction of diphenyldiazomethane with allyl acetate. Benzophenone. The opaque, dirty-white first and second fractions of the condensation product with n_D^{16} 1.594-1.591 partly crystallized on keeping. The crystals were filtered off and sucked free from the residual uncrystallized portion (5.9 g) which was a transparent, colorless oil with n_D^{16} 1.5745 (compare n_D^{16} for the third fraction in section I above). The crystals melted at 43-46°, and after one recrystallization from alcohol they melted at 48-49°.

They were identical with authentic benzophenone (mixed melting test). Yield 7.35 g or 3.5% of theory, calculated on the original diphenyldiazomethane.

The crystals melting 157-158° had a light-yellow color and were difficultly soluble even in hot alcohol, easily soluble in ether, and still more easily in benzene. It was impossible to raise the melting point either by repeated crystallizations from alcohol-benzene or by substitution of solvent (benzene, ether). Nitrogen determinations, however, gave results corresponding to the formula for ketazine and a mixed sample with authentic ketazine (m. pt. 162°) melted without depression (at 160°).•

Found %: N 7.95, 7.62; M 366.2. $C_{26}H_{20}N_2$. Calculated %: N 7.78; M 360.3.

Hydrolysis of the crystals melting at 157-158° with sulfuric acid. 1 g of the substance and 150-200 ml 20-30% sulfuric acid were boiled for many hours under a reflux condenser until the crystals had gone completely into solution. The solution (with a thin layer of yellow oil floating on its surface) was then steam-distilled. From the distillate of the ether extraction was obtained 0.57 g (57% of theory••) benzophenone with m. pt. 46-47°, which rose after recrystallization from alcohol to 48-49° and did not depress the m. pt. of an authentic sample. The solution remaining in the distillation flask was filtered from a small amount of solid precipitate which, after drying, weighed 0.16 g and melted at about 206°. This solid was very difficultly soluble in alcohol and rather more soluble in benzene. After crystallization from alcohol-benzene it melted at 207.5°. This melting point remained constant.

Hydrolysis (in the above-described manner) of the crystals melting at 157-158° with 20% sulfuric acid gave 0.75 g of slightly yellowish crystals melting at 207.5° (after one crystallization from alcohol-benzene). Further crystallization gave 0.63 g of colorless crystals with the same melting point. A qualitative test for nitrogen by Lassaigne's method gave a negative result, while analysis gave results fairly close to those calculated for tetraphenylethane (the literature gives m. pt. 209° [7]).

Found %: C 92.90, 92.92; H 6.68. 6.93. $C_{26}H_{22}$. Calculated %: C 93.14; H 6.86.

For comparison, authentic tetraphenylethane was prepared by the action of granulated zinc on diphenylbromomethane dissolved in dry ethylacetoacetate [8]. M. pt. 206°. No depression of melting point when mixed with the investigated preparation.

The sulfuric acid filtrate from the tetraphenylethane prepared by hydrolysis of 1 g crude ketazine with m. pt. 157-158° was concentrated on the water baths, and then cooled to separate 0.1 g hydrazine sulfate with m. pt. 254-258° (with decomposition) [4]; yield 28% of theory based on the formula of ketazine.

Hydrolysis of authentic ketazine. Heating of 1 g ketazine (m. pt. 162°) in 30% sulfuric acid gave benzophenone with m. pt. 48-49° (0.59 g or 59% of the theoretical yield) and hydrazine sulfate with m.p. 255° with decomp.) (0.31 g or 86% of theory). Tetraphenylethane was not found among the hydrolysis products. The same data (without indication of yields) were reported by Curtius [4].

Crystals with m. pt. 172-173°. As already pointed out in section I above, crystals melting at 172-173° were obtained after 2-3 recrystallizations of the substance, separating in the first operation, on dilution of the crude condensation product with alcohol. Weight 1.4 g. After crystallization, the color of the crystals and the solubility were approximately the same as those of the crystals with m. pt. 157-158°. A mixed sample with authentic ketazine (m. pt. 162°) gave a depression of m. pt. (154-155°). Determinations of nitrogen and of the molecular weight did not permit a choice to be made between the formulas $C_{26}H_{22}N_2$ and $C_{26}H_{20}N_2$.

0.1220 g substance: 8.15 ml N_2 (18°, 744 mm). 0.1085 g substance; 9.39 g benzene: Δt 0.170°. Found: % N 7.85; M 349.4. $C_{26}H_{22}N_2$. Calculated %: N 7.73; M 362.3. $C_{26}H_{20}N_2$. Calculated %: N 7.78; M 360.3.

Hydrolysis of the crystals with m. pt. 172-173°. After heating with 30% sulfuric acid, 1 g of substance yielded 0.42 g benzophenone with m. pt. 43-44° (not recrystallized), 0.35 g tetraphenylethane with m. pt. 207° (not recrystallized) and 0.07 g hydrazine sulfate.

IV. Condensation of ethyl diazoacetate with allyl acetate. Ethyl diazoacetate was purified by distillation with steam. The catalyst, copper sulfate, was dehydrated at 170-180°. Into a round-bottomed flask, fitted with a mercury seal and stirrer, a dropping funnel and a reflux condenser, was charged 380 ml allyl acetate and 2 g anhydrous copper sulfate; in the dropping funnel was placed a solution of 136.9 g ethyl diazoacetate in 136 ml allyl acetate. The allyl acetate in the flask was heated to boiling, after which with energetic stirring the solution in the

• Authentic ketazine was prepared by the action of iodine in alcoholic solution on benzophenone hydrazone [4].

•• Calculated on the gross formula of $C_{26}H_2ON_2$ for the substance melting at 157-158°.

dropping funnel was slowly added. Even after only a few drops had been run in, the contents of the flask turned grey; with further addition the color changed to nearly black. The nitrogen evolved during the reaction was collected in a gasholder. At the end of the experiment 25.24 l nitrogen (normal conditions) had been collected, equivalent to 93.8% of the theoretical amount. After 20-30 minutes the evolution of nitrogen usually ceased (indication of end of reaction). After cooling and filtering off the catalyst, the excess allyl acetate was distilled off from the solution in vacuum (130 mm). The residue in the distillation flask was distilled in a 1 mm vacuum. Nearly the whole of the condensation product came over within the range of 83-86° at 1 mm. Yield 57.7 g or 70.6% of theory, calculated on the formula of ester (III), $C_9H_{14}O_4$. B. pt. 111-114° (10 mm); 92-95° (3 mm); 83-85° (1 mm); $d_4^{19.9}$ 1.078; d_4^{18} 1.079; $n_D^{19.9}$ 1.4422; n_D^{18} 1.4431.

0.1422 g substance: 0.3173 g CO_2; 0.1060 g H_2O. Found %: C 58.00; H 7.94. $C_9H_{14}O_4$. Calculated %: C 58.06; H 7.57.*

With the aim of reducing the amount of resin in the reaction products, we tried to perform the reaction at a temperature much below the boiling point of allyl acetate, but without success. Thus in one experiment the ethyl diazoacetate was run in at a reaction mixture temperature of 65-70°. In this case nitrogen, as a rule, was not evolved, and the solution retained its yellow-green color, indicating the presence of undecomposed ethyl diazoacetate. After a few grams of ethyl diazoacetate had been added to the solution, for no apparent reason a violent and exothermic decomposition of the diazoacetate set in, accompanied by ejection of part of the solution through the seal and condenser. The temperature of the solution suddenly rose to 103° and the color darkened.

183 g crude ester (III) was treated in the cold with 3% potassium permanganate (14.9 g) until the violet color of the solution had disappeared. After filtration of the manganese dioxide, which was carefully washed with ether, the ester (III), separating as a colorless oil in the filtrate, was separated from the aqueous layer and the latter was extracted with ether. The combined ether extracts were mixed with ester (III), the solution dried with $CaCl_2$, and after driving off the solvent the ester (III) was distilled in vacuum. Yield of analytically pure preparation 162.9 g (88.7 % of theory). B. pt. 128-129° (22 mm); 106-107° (8 mm); 76-77° (0.5 mm); $d_4^{18.8}$ 1.079; $n_D^{18.8}$ 1.4429; MR_D 45.74; calculated. 44.85; exaltation: 0.19.

0.2272 g, 0.1117 g substance: 0.4888 g, 0.2373 g CO_2; 0.1587 g, 0.0767 g H_2O. Found %: C 58.19, 57.95. H 7.82, 7.68. $C_9H_{14}O_4$. Calculated %: C 58.06; H 7.57. 0.1836 g, 0.1851 g substance: 16.82 g, 22.96 g benzene; Δt 0.300°, 0.225°. Found: M 186.7, 183.9. $C_9H_{14}O_4$. Calculated: M 186.2.

Raman spectrum of ester(I) was measured with the help of a Zeiss triprism spectrograph, using a mercury lamp (wave length λ 4358.3 A) as source of excitation; slit 0.1 mm; time of exposure 6 hours. Light filter: hard glass. Results of measurements of spectrum of ester (III): 636.4 (3), 746(3), 840.9(1), 862.2(2), 889.7(2), 1033.4(2), 1098.9(2), 1118.5(2), 1202.9(3), 1455(5), 1728.7(3), 2948(5), 3137(4).

The manganese dioxide obtained during the oxidation was twice extracted with boiling water and the wash liquors combined with the aqueous solution previously separated from the layer of purified ester (III). From the combined solutions the volatile and volatile-in-steam organic acids were separated in the usual manner. The aqueous distillate contained 0.95 g (estimated by alkali titration) of acid and in the solution of nonvolatile acids was found 3 g of oxalic acid whose identity was confirmed by analysis of the calcium salt.

Found %: Ca 27.70, 27.45. $C_2O_4Ca \cdot H_2O$. Calculated %: C 27.30.

VI. Trans-2-(hydroxymethyl)-cyclopropane-1-carboxylic acid (IV). Saponification of the cyclic ester (III) for the purpose of preparing 2-hydroxymethyl-cyclopropane carboxylic acid was effected by various methods, including the action of a methyl alcoholic solution of potassium hydroxide, the action of aqueous solutions of potassium hydroxide, and the action of barium hydroxide. The best yields could be obtained by the following procedure.

Into a three-liter round-bottomed flask fitted with a stirrer and a reflux condenser was charged 186 g (1 mole) cyclic ester (III) and 1400 ml of 2N solution of potassium hydroxide. The reaction mixture was boiled with stirring until the originally turbid solution had become transparent. After cooling, the excess of alkali was neutralized to phenolphthalein with 2 N sulfuric acid (the ratio of the volumes of solutions of alkali and acid determined by titration to phenolphthalein was 25 ml 2N KOH to 20.2 ml of 2 N H_2SO_4). 66 ml of 2 N H_2SO_4 was consumed,

* If we assume that 3% ethyl fumarate is contained in ester (III), then the calculated C and H contents of the crude preparation are respectively 57.93 and 7.48%.

equivalent to 82 ml of 2N solution of excess KOH. The neutral solution was then concentrated on the water bath to a volume of about 300 ml, and to this solution was added 1000 ml 2N H_2SO_4 – an amount nearly sufficient for complete separation in the free state of both of the organic acids (the theoretical requirement is 1065 ml 2N H_2SO_4). The acidified solution was concentrated in vacuum to a volume of 200 ml prior to removal by steam-distillation of the main bulk of ethyl acetate formed in the hydrolysis. The residue of acetic acid was removed from the solution by steam-distillation at the ordinary pressure. The solution was then acidified for the last time (70-100 ml 2N H_2SO_4) and transferred to a Soxhlet apparatus for ether extraction of the cyclic acid.

After extraction for several days (the acid is sparingly soluble in ether and readily soluble in water), the ether was evaporated off and the residual oily acid was kept in a vacuum, first at room temperature and then at 50-60°; in this way the remaining ether, water and acetic acid were removed. The acid dried in this manner is a pale-yellow, very viscous oil. Yield 92.8 g or 80% of theory calculated on the ester (III). On prolonged standing in the desiccator it gradually crystallizes, but not completely, a portion remaining as an oil. In the experiment here described, the crystallized acid was filtered off at the pump to get rid of the oil and the crystals washed on the filter with a small quantity of cold ether. After keeping on a porous porcelain plate the crystals were freed from the last traces of adsorbed oil. The solid acid was a white, bulky powder melting at 63°. Weight 57.6 g. By the method described blow the separated oil yielded a further 7 g solid acid melting at 62-64°. Consequently the total yield of crystalline trans-(2)(hydroxymethyl)-cyclopropane-1-carboxylic acid was 64.6 g or 55.7% of theory. The acid was obtained in the analytically pure form after a single recrystallization from a mixture of ether and petroleum ether. M. pt. 64-65°.

0.2794 g, 0.1761 g substance: 32.3 ml, 20.3 ml 0.1 N. NaOH (factor 0.7456). 0.1301 g, 0.1312 g substance: 0.2459 g, 0.2495 g CO_2; 0.0830 g, 0.0846 g H_2O. Found. equiv. 116.1% C 51.72; H 6.94.

Oxidation of acid (IV). 5.8 g (0.05 mole) of acid, dissolved in a little water, was treated in the cold with the calculated amount (10.5 g = 0.066 mole) of potassium permanganate used in the form of 30% solution. After working up in the usual manner, the aqueous solution of the oxidation products was concentrated to a volume of 40-50 ml, acidified with 3 ml concentrated sulfuric acid, and extracted with ether in the Soxhlet.

The ether extract yielded 5.5 g (84.6% of theory) of crystalline trans-2-cyclopropane-1,2-dicarboxylic acid with m. pt. 173° (175° after crystallization from water), in agreement with the literature [7].

Found %: C 46.32; H 4.99; equiv. 64.89, 64.88. $C_3H_4(CO_2H)_2$. Calculated %: C 46.17; H 4.75; equiv. 65.05.

There was no melting point depression in admixture with a preparation of the same acid obtained by another route [1].

VII. Lactone of cis-2-(hydroxymethyl)-cyclopropane-1,2-dicarboxylic acid (V). 28 g of the oily acid filtered off, as above, from the solid acid (IV), was subjected to supplementary drying by keeping in a 10 mm vacuum, first at 60° and then at 90°. This operation likewise failed to cause crystallization. An attempt was then made to distil the liquid acid in a 2 mm vacuum. This distillation yielded (from 24 g liquid acid) 7.1 g of colorless distillate boiling at 62-72° (1.5-2.5 mm), leaving 16.3 g residue which crystallized on standing. Pressing on a porous plate followed by recrystallization from ether-petroleum ether mixture gave 7 g of trans-2-(hydroxymethyl)-cyclopropane-1-carboxylic acid with m. pt. 62-64°. Following a second distillation, the main portion of the distillate had b. pt. 66-70° (2 mm) and its analysis corresponded to that of lactone (V): d_4^0 1.199; d_4^{20} 1.180; n_D^{20} 1.4652; MR_D 23.00; calculated 23.24.

0.1464 g, 0.1340 g substance: 0.3278 g, 0.3055 g CO_2; 0.0824 g, 0.800 g H_2O. 0.1654 g, 0.2074 g substance; 17.17 g, 16.70 g benzene: Δt 0.47°, 0.60°. Found %: C 61.05, 60.81; H 6.30, 6.53; M 105.4, 106.4. $C_6H_6O_2$. Calculated %: C 61.22; H 6.17; M 98.1.

The lactone is not attacked by 0.1 N caustic alkali solution on momentary contact. In the cold the alkali is slowly consumed; on heating with excess 0.1 N alkali solution the lactone ring is quickly ruptured. Below are presented data for molecular weight determination of lactone (V) by the back-titration method (using phenolphthalein): 0.1803 g, 0.1784 g substance: 50 ml, 50.2 ml 0.1 N. NaOH (factor 0.7285); 16.35 ml, 16.70 ml 0.1 N. HCl (factor 1.083). Found: M 96.36, 96.61. $C_6H_6O_2$. Calculated: M 98.11.

Raman spectrum of lactone (V): 185(6), 243(4), 378(4), 478(5), 558(1), 613(9), 648(2), 705(10), 780(6), 829(5), 850(9), 899(4), 952(8), 975(6), 994(4), 1038(2), 1055(2), 1112(3), 1171(7), 1220(2), 1309(3), 1344(4), 1373(1), 1450(3), 1481(4), 1760(6W), 2910(5), 2981(4), 3002(5), 3085(8).

The spectrum of the lactone was recorded with an ISP-51 triprism spectrograph. Slit width 0.04 mm. Exposure period 6 hours. Glass light filter; Hg 436. Intensities were evaluated photometrically.

Oxidation of lactone (V). To 3.95 g (0.04 g-mole) lactone was added a solution of 2.25 g (0.04 g-mole) potassium hydroxide in 20 ml of water, and the resultant solution of potassium salt of acid (IVa) was treated, first in the cold and then on the water bath, with the calculated amount (8.45 g) potassium permanganate in the form of a 3% solution. After working up in the usual manner, the cis-cyclopropane-1,2-dicarboxylic acid was separated from the acidified solution by ether extraction. Yield 3.12 g (0.024 g-mole, 60% of the theoretical yield). After two crystallizations from water it melted at 138-139° [9].

Found %: C 45.90, 45.77; H 4.77, 5.01; equiv. 65.75, 65.67. $C_3H_4(CO_2H)_2$. Calculated %: C 46.17; H 4.65; equiv. 65.05.

SUMMARY

1. It is shown that reaction of diphenyldiazomethane with allyl acetate results in a 55% yield of 1-acetoxymethyl-2,2-diphenylcyclopropane, which on alkaline hydrolysis gives the previously investigated 1-hydroxymethyl-2,2-diphenylcyclopropane.

2. By-products of the first-mentioned reaction are benzophenone, ketazine (tetraphenylazimethylene) and a product of similar structure to ketazine which on alkaline hydrolysis yields tetraphenylethane, benzophenone and hydrazine sulfate.

3. Reaction of ethyl diazoacetate with allyl acetate in presence of copper sulfate leads to formation in 70% yield of 2-(acetoxymethyl)-cyclopropane-1-carboxylic acid together with an insignificant amount of ethyl fumarate.

4. Alkaline hydrolysis of 2-(acetoxymethyl)-cyclopropane-1-carboxylic acid is shown to yield a mixture of the trans- and cis-forms of the corresponding cyclic hydroxy acid; the trans-isomer can be isolated from the mixture, and the cis-form can be converted into the lactone by heating.

5. By oxidation of the trans-isomer of the acid it is possible to obtain transcyclopropane-1,2-dicarboxylic acid in a yield of 84% of theory; oxidation of the lactone gives the cis-form of the acid in 60% yield.

6. The structures of the cyclic ester and of the bicyclic lactone were confirmed by data for the Raman spectra of these compounds.

LITERATURE CITED

[1] Dyakonov and Pirogova, J. Gen. Chem., 21, 1979 (1951); see Consultants Bureau translation, p. 2201.

[2] Dyakonov, J. Gen. Chem., 21, 1986 (1951); see Consultants Bureau translation, p. 2209.

[3] Staudinger, Anth. and Pfenninger, Ber., 49, 1928 (1916).

[4] Curtius, Rauterberg, J.prak.Chem., [2] 44, 200 (1891).

[5] Organic Synthesis, 24, 53 (1944).

[6] Swanson and Coss, Proc. Iowa. Acad. Sci., 45, 123, (1938).

[7] Beilstein's Handbuch of Org. Chem., IV Aufl.

[8] Norris, Thomas, Brawn, Ber., 43, 2959 (1910).

Received January 31, 1951

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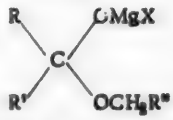
STERIC HINDRANCE IN ORGANOMAGNESIUM REACTIONS

XII. THE REACTION OF DIMETHYL OXALATE WITH DI-ortho -SUBSTITUTED ARYL MAGNESIUM HALIDES

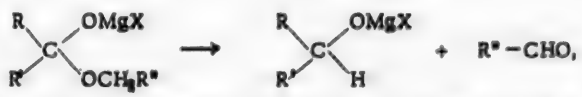
I. I. Lapkin, N. K. Ponomareva and L. Yu. Pinegina

In a previous communication [1] a study was made of the cause and mechanism of the reductive reactions which take place when esters react with organomagnesium compounds.

The stability of the initially formed compound



depends both on the character of the radicals R and R' and on the character of the alkoxyl group. The more electrophilic are radicals R and R', the less stable is the compound. The stability may be reduced to such an extent on heating at 40-42° (the boiling point of the ethereal solution) that the compound decomposes according to the equation:



which also involved reduction. The decomposition is naturally possible if the esters are formed with primary and secondary alcohols. Thus the esters of oxalic acid containing both primary and secondary alkoxyl groups form esters of secondary α-hydroxy acids [2,3] on reacting with ortho-substituted aryl magnesium halides and with branched alkyl magnesium halides.

As was pointed out in the same paper [1], the only exception is the dimethyl ester of oxalic acid which when reacted with equivalent amounts of di-ortho-substituted aryl magnesium halides forms methyl esters not of α-hydroxy acids but the normal products of the first stage of the reaction – methyl esters of α-keto acids.

This difference, however, is not fundamentally significant, as will be demonstrated in the present paper. The difference only resides in the higher thermal stability of the magnesium complex formed with the above compounds; its decomposition calls for a much higher temperature (100°).

Under these conditions dimethyl oxalate and methyl magnesium bromide form the methyl ester of 2,4,6-trimethylmandelic acid (experiment 1). Under the stated conditions dimethyl oxalate and duryl, isoduryl and pentamethylphenyl magnesium bromides similary react to form, respectively (experiments 2,3,4), the methyl esters of 2,3,5,6-tetramethyl, 2,3,4,6-tetramethyl and pentamethylmandelic acids (I).

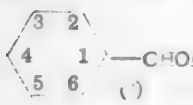
In connection with the reaction of the methyl ester of oxalic acid with sterically hindered organomagnesium compounds, we must take account of still another feature – the occurrence in large measure of saponification which results in the formation of a relatively large amount of magnesium oxalate.

In general, as shown previously (1,2), the formation of esters of secondary α-hydroxy acids with the help of esters of oxalic acid is nearly always accompanied to some degree by the side reaction of saponification of these esters, probably in accordance with the equation put forward by Stadnikov [4] and Zalkind [5]. The possibility is not excluded of saponfication proceeding by another route, similar to the alkylation of esters with sulfuric acids and sulfo acids. Cases are even known of the formation of esters of organic acids by such a method. For example, Gilman and Robinson [6] found that allyl benzoate and phenyl magnesium bromide

form a small quantity of allylbenzene, while Arnold [7] obtained 57% of allylmesitylene with the help of the same ester.

With the majority of the esters of oxalic acid the saponification reaction proceeds to a minor degree, but with diphenyl and dimethyl esters this side reaction becomes the principal one. Experiments with various esters of oxalic acid and mesityl magnesium bromide have yielded the following esters with the degrees of saponification shown: Diphenyloxalate – 80%, dimethyl oxalate – 40%; diethyl oxalate – 16%; di-n-butyl oxalate – 10%; diisobutyl oxalate – 9%; diisopropyl oxalate – 6%.

The above figures show that the degree of saponification depends on the character of the radicals of the alkoxyl group entering into the composition of the oxalic acid esters. The more electronegative is the radical, the greater the degree of this reaction. The radicals concerned can thus be arranged in the following order of electronegativity:



(I)

$C_6H_5- > CH_3- > C_2H_5- > n\text{-}C_4H_9- > iso\text{-}C_4H_9- > iso\text{-}C_3H_7-$.

This order agrees entirely with that of Norris [8] and Kharasch [9].

The saponifying tendency of the methyl and phenyl esters of oxalic acid can be exploited for the development of a rather interesting method of synthesis of di-ortho-substituted arylglyoxalic acids. Although magnesium oxalate does not, as our experiments showed, react with aryl magnesium halides either under the usual temperature conditions employed for organomagnesium reactions or at much higher temperatures (100°), it was to be expected that at the instant of its formation this salt would be more active and on reaction with di-ortho-substituted aryl magnesium halides it would form the magnesium salt of the arylglyoxylic acids.

The formation of arylglyoxylic acids might be explained by the possibility of saponification of the already formed esters of the arylglyoxylic acids with magnesium bromide, but this possibility is ruled out because it has been experimentally shown that esters of mesitylglyoxylic acid are not saponified by magnesium bromide at 100°.

With dimethyl oxalate under the stated conditions, mesityl, duryl, isoduryl and pentamethylphenyl magnesium bromides form, respectively, 2,4,6-trimethylphenyl, 2,3,5,6-tetramethylphenyl, 2,3,4,6-tetramethylphenyl and pentamethylphenylglyoxylic acids with yields of 30-20% (experiments 1, 2, 3 and 4). In the case of monosubstituted aryl magnesium halides it was not found possible to effect the reaction in such a manner.

Consequently three products are formed by reaction of dimethyl oxalate with di-ortho-substituted aryl magnesium halides at an elevated temperature (100°): Methyl esters of arylglycolic acids, arylglyoxylic acids, and the magnesium salt of oxalic acid. In view of the fact that the arylglyoxylic acids are obtained in a fairly pure form, the method can be recommended for the preparation of these acids.

EXPERIMENTAL

1. Reaction between mesityl magnesium bromide and dimethyl oxalate at high temperature (ratio of 1:1). To a solution in ether of 30 g dimethyl oxalate (0.25 mole) is gradually added an ethereal solution of mesityl magnesium bromide prepared from 50 g mesityl bromide (0.25 mole) and 6.5 g magnesium. After the mixing of the reaction components the ethyl ether was replaced by toluene and the reaction mixture then heated for 20 hours on a boiling water bath, after which it was decomposed with water and 10% hydrochloric acid. Following the removal of the aqueous layer, the toluene solution was washed with water, with 10% sodium carbonate and again with water until the reaction was neutral, and then dried with calcined sodium sulfate. Finally, after distilling off the toluene, the residual mixture of substances was distilled in vacuum. The main fraction (130-145° at 6 mm, 6 g) was dissolved in petroleum ether (boiling up to 70°) and cooled. The separated crystals of the methyl ester of 2,4,6-trimethylmandelic acid were purified by recrystallization from the same solvent until the m. pt. was constant at 90-91°.

0.1076 g substance: 0.2722 g CO_2; 0.0757 g H_2O. Found %: C 69.23; H 7.89. $C_{12}H_{16}O_3$. Calculated %: C 69.22; H 7.75. 0.1678 g substance: 18.3 ml CH_4 (20°, 754 mm). Found %: OH 7.6. $C_{12}H_{16}O_3$. Calculated %: OH 8.1.

The literature [10] gives the m. pt. of the ester as 90-91° and 91-92°.

The soda solution was washed twice with ether and then acidified with hydrochloric acid; the resultant yellow crystals of 2,4,6-trimethylphenylglyoxylic acid were washed with cold water, dried, and purified by a single recrystallization from petroleum ether-toluene mixture. M. pt. 115-116°. Yield 12.5 g (25%).

0.1153 g substance: 0.2915 g CO_2; 0.0665 g H_2O. Found %: C 68.99; H 6.45. $C_{11}H_{12}O_3$. Calculated %: C 68.71; H 6.30. 0.1939 g substance: 23.6 ml CH_4 (20°, 754 mm). Found %: active H 0.50. $C_{11}H_{12}O_3$. Calculated %: active H 0.52.

In the literature [10] this acid is stated to melt at 116, 118°.

An increased yield of this acid did not result from raising the temperature of heating of the reaction mixture to 140°.

2. Reaction between duryl magnesium bromide and dimethyl oxalate at a high temperature (ratio 1:1). As in the preceding experiment, addition to the ether solution of dimethyl oxalate was made of an ether solution of duryl magnesium bromide (0.1 mole) prepared under the previously described conditions [2]. After the reactants had been mixed the ether was replaced by toluene and the mixture heated on the boiling water bath for 20 hours. Decomposition of the magnesium complex was effected with water and 20% hydrochloric acid. Treatment of the toluene layer (10%) with soda solution brought down the sodium salt (sparingly soluble in water) of 2,3,5,6-tetramethylphenylglyoxylic acid which was filtered off, washed with ether and dried.

Decomposition of this salt with 10% hydrochloric acid yielded light-yellow crystals of 2,3,5,6-tetramethylphenylglyoxylic acid (7.5 g, 36% yield), which were washed with water and dried prior to purification by recrystallization from a mixture of petroleum ether and toluene until the melting point was constant at 125-126°.

0.1097 g substance: 0.2802 g CO_2; 0.0676 g H_2O. Found %: C 69.69; H 6.90. $C_{12}H_{14}O_3$. Calculated %: C 69.88; H 6.84. 0.1297 g substance: 14.2 ml CH_4 (17.5°, 762 mm). Found %: active H 0.46. $C_{12}H_{14}O_3$. Calculated %: active H 0.48.

A m. pt. of 124° is reported for 2,3,5,6-tetramethylphenylglyoxylic acid in the literature [10].

The toluene solution was washed with water and dried. Distillation gave a fraction (2.75 g) at 145-165° at 8 mm which was dissolved in an equal amount of petroleum ether and cooled. The resultant crystals of the methyl ester of 2,3,5,6-tetramethylmandelic acid were purified by further recrystallization from the same solvent until the melting point was constant at 119-120°.

0.1173 g substance: 0.3010 g CO_2; 0.0861 g H_2O. Found %: C 76.02; H 8.21. $C_{13}H_{18}O_3$. Calculated %: C 70.24; H 8.16. 0.1245 g substance: 11.6 ml CH_4 (17.5°, 766 mm). Found %: OH 6.74. $C_{13}H_{18}O_3$. Calculated %: OH 7.60.

This ester has not been described in the literature.

3. Reaction of dimethyl oxalate with duryl magnesium bromide at high temperature (ratio of 1:1). This reaction was performed with the same amounts of components (0.25 mole each) and under the same conditions as in experiment 1.

After distillation, from the toluene solution was obtained a fraction (4 g) at 140-185° (11 mm).

A narrower cut of this fraction (155-165° at 11 mm) was collected (3 g). It was dissolved in petroleum ether and cooled. The separated crystals of the methyl ester of 2,3,4,6-tetramethylmandelic acid were purified by recrystallization. M. pt. 80-81°.

0.1201 g substance: 0.3081 g CO_2; 0.0869 g H_2O. Found %: C 70.01; H 8.10. $C_{13}H_{18}O_3$. Calculated %: C 70.24; H 8.16.

There was separated from the soda solution, by the previously described method, liquid 2,3,4,6-tetramethylphenylglyoxylic acid in the amount of 14 g (25%). Reduction of this acid with sodium amalgam in aqueous alcoholic solution yielded 2,3,4,6-tetramethylmandelic acid with m. pt. 153°. The literature [10] gives 156°.

4. Reaction of dimethyl oxalate with pentamethylphenyl magnesium bromide at high temperature (ratio of 1:1). Since neither pentamethylphenyl bromide nor the dibromide reacted completely with magnesium, the ether solution of pentamethylphenyl magnesium bromide was prepared under the previously described conditions [2], i.e., in presence of an equivalent amount of ethyl bromide.

The so-prepared ethereal solution of pentamethylphenyl magnesium bromide (0.25 mole) was gradually poured into an ethereal solution of 44 g of dimethyl oxalate. After mixing, the ether was replaced by toluene, and the reaction mixture heated on the boiling water bath for a period of 20 hours. Further treatment of the mixture was as in the previous experiments.

The main fraction of 6 g (140-150° at 6 mm) was dissolved in petroleum ether and cooled. The crystals of methyl pentamethyl mandelate were purified by recrystallization from the same solvent. M. pt. 128-129°.

0.1101 g substance: 0.2865 g CO_2; 0.0847 g H_2O. Found %: C 71.00; H 8.61. $C_{14}H_{20}O_3$. Calculated %: C 71.16; H 8.53. 0.1212 g substance: 11.4 ml CH_4 (18°, 758 mm). Found %: OH 6.7. $C_{14}H_{20}O_3$. Calculated %: OH 7.2

The ester has not been described in the literature.

The soda solution was twice washed with ether and then acidified with 10% hydrochloric acid. The resultant yellow crystals of pentamethylphenylglyoxylic acid were purified by recrystallization from toluene. M. pt. 131-132° (yield 20%).

The literature gives a melting point of 122 (from hot alcohol).

0.1136 g substance: 0.2941 g CO_2; 0.0738 g H_2O. Found %: C 70.72; H 7.28. $C_{13}H_{16}O_3$. Calculated %: C 70.80; H 7.32.

SUMMARY

1. A study has been made of the reaction of dimethyl oxalate with equivalent amounts of di-ortho-substituted aryl magnesium bromides. New experimental material has confirmed the validity of the previously proposed mechanism of the reductive reactions which sometimes take place when esters react with organomagnesium compounds.

2. A method is suggested for the preparation of di-ortho-substituted arylglyoxylic acids in a yield of up to 25-30%.

LITERATURE CITED

[1] I. I. Lapkin, J. Gen. Chem., 17, 1339 (1947).

[2] I. I. Lapkin, J. Gen. Chem., 16, 721 (1946); 17, 1332 (1947).

[3] I. I. Lapkin and A. V. Lyubimova, J. Gen. Chem., 18, 701 (1948).

[4] G. L. Stadnikov, Anomalous Grignard reactions, p. 81 (Odessa, 1916).

[5] Yu. S. Zalkind, J. Russ. Chem. Soc., 46, 692 (1914).

[6] H. Gilman and I. D. Robinson, Chem. Zentr., II, 2554 (1929).

[7] R. T. Arnold, R. Liggett and S. Scarles, J. Am. Chem. Soc. 70, 3938 (1948).

[8] See C. D. Hurd, Pyrolysis of Carbon Compounds, p. 30 (Moscow, 1938).

[9] M. Kharasch and Flenner, J. Am. Chem. Soc., 54, 674 (1932).

[10] Beilstein.

Received June 17, 1950

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STERIC HINDRANCE IN ORGANOMAGNESIUM REACTIONS

XIII. PREPARATION OF KETONES BY REACTION OF ACID HALIDES WITH ORGANOMAGNESIUM COMPOUNDS

I. I. Lapkin, N. I. Latosh and E. S. Belov

In one of the previous communications [1] it was pointed out that the existing belief in the impossibility of obtaining ketones by reaction of organomagnesium compounds with halides of monocarboxylic acids only holds good for a relatively small group of low-molecular organomagnesium compounds and acid halides when both components are free from steric hindrance. This is not true of the other groups of these compounds. If in one of the reactants the structure is such as to cause steric hindrance, then the formation of ketones by the reaction in question is quite feasible.

On the basis of the reaction of acetyl and benzoyl chlorides with organomagnesium compounds it was shown that di-ortho-substituted aryl magnesium bromides form only ketones, regardless of the reaction conditions, while mono-ortho-substituted magnesium complexes only yield ketones as the sole product if certain conditions are observed.

The investigations described in the present paper had the objective, firstly, of showing with the help of a large amount of experimental material that the conclusions previously reached were generally valid, and, secondly, of elucidating the influence of the character of the radicals and halides entering into the composition of acid chlorides upon the course of the reaction and the quantitative yield of ketones.

The reactants selected for investigation were, on the one hand, aryl magnesium halides variously substituted in the ortho-position (and thus with varying degrees of steric hindrance) and, on the other hand, chlorides of isovaleric, butyric and isobutyric acids.

Mesityl magnesium bromide reacts with the above chlorides to form isobutyl, propyl and isopropyl mesityl ketones under any reaction conditions (i.e. regardless of the ratio of components, the order of their mixing and the duration of heating).

In contrast to the di-ortho-substituted compounds, the mono-ortho-substituted aryl magnesium halides, particularly o-tolyl magnesium bromide, and also α-naphthyl magnesium bromide whose second ring can be arbitrarily regarded as one ortho-substituent, manifest insufficient hindrance to permit the reaction to be stopped at the stage of ketone formation. Conditions favoring stoppage at the required stage must be created, and then ketones are likewise the sole reaction products. As previously shown [1], such conditions are: Mixing of the reaction components in equimolar amounts, the addition of the Grignard reagent to the cooled ethereal solution of the acid chloride. Under these conditions o-tolyl magnesium bromide and α-naphthyl magnesium bromide react with the chlorides of butyric, valeric and isobutyric acids to form exclusively ketones.

It was impossible to obtain ketones, however, from aryl magnesium halides not substituted in the ortho-position even when the reaction mixture was rather intensively cooled (down to −15°). Formation occurs, side by side with ketones, of products of the second stage of reaction – tertiary alcohols. • Results are presented in Table 1.

The data of Table 1 demonstrate that the yield of ketones is greatly influenced by the nature of the radicals of the halides of monocarboxylic acids. This effect is further illustrated by the data set out in Table 2 in which the percentage yields of ketones are arranged in order of increasing magnitude; the figures in brackets are the yields of dehydration products (tertiary alcohols).

The gradual increase in the ketone yields in the order shown in the table is explained by the fact that the

• In practice not tertiary alcohols but products of their dehydration (unsaturated hydrocarbons) are formed.

TABLE 1

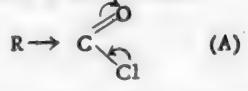
No.	Reaction	Ratio	Ketone	Yield of ketone (%)	Yield of unsat. hydrocarbon (%)
1	Mesityl magnesium bromide + isovaleryl chloride	1:1	Isobutyl mesityl ketone	20	–
2	Mesityl magnesium bromide + isovaleryl chloride	2:1	Isobutyl mesityl ketone	39	–
3	o-Tolyl magnesium bromide + isovaleryl chloride	1:1	Isobutyl o-tolyl ketone	46	–
4	α-Naphthyl magnesium bromide + isovaleryl chloride	1:1	Isobutyl α-naphthyl ketone	52	–
5	p-Tolyl magnesium bromide + isovaleryl chloride	1:1	Isobutyl p-tolyl ketone	39	13
6	Phenyl magnesium bromide + isovaleryl chloride	1:1	Isobutyl phenyl ketone	32	28
7	Mesityl magnesium bromide + butyryl chloride	1:1	Propyl mesityl ketone	18	–
8	Mesityl magnesium bromide + butyryl chloride	2:1	Propyl mesityl ketone	37	–
9	o-Tolyl magnesium bromide + butyryl chloride	1:1	Propyl o-tolyl ketone	42	–
10	α-Naphthyl magnesium bromide + butyryl chloride	1:1	Propyl α-naphthyl ketone	51	–
11	Phenyl magnesium bromide + butyryl chloride	1:1	Propyl phenyl ketone	27	24
12	Mesityl magnesium bromide + isobutyryl chloride	1:1	Isopropyl mesityl ketone	45	–
13	Mesityl magnesium bromide + isobutyryl chloride	2:1	Isopropyl mesityl ketone	55	–
14	o-Tolyl magnesium bromide + isobutyryl chloride	1:1	Isopropyl o-tolyl ketone	53	–
15	α-Naphthyl magnesium bromide + isobutyryl chloride	1:1	Isopropyl α-naphthyl ketone	65	–
16	Phenyl magnesium bromide + isobutyryl chloride	1:1	iso-Propyl phenyl ketone	42	20

TABLE 2

Acid chloride	Aryl magnesium bromide			
	Mesityl	o-Tolyl	α-Naphthyl	Phenyl
Acetyl•	10	30(14)	50(2.5)	19(22)
Butyryl	18	42	51	27(24)
Isovaleryl	20	46	52	32(28)
Isobutyryl	45	53	65	42(20)

• The data for the quantitative yield of ketones due to reaction of acetyl chloride with the aryl magnesium bromides are taken from a preceding paper.

inductive repulsion of electrons by the radicals is intensified in the following order [2,3]: Isopropyl > isobutyl > propyl > methyl. Furthermore an intensification occurs, in the same order, of the statistical effect of conjugation in the acid chlorides in question (A):



(A)

This intensification of effect overlaps that supplementary hindrance which is created by the increased length of the radical chains in the acid chlorides and which is the cause of the gradual rise in ketone yields in the order specified. This rise, however, can only continue to a certain limit. Further increase in length and branching of the chain of the radicals will be accompanied by intensification of the steric hindrance which, of course, results in a fall in the yields of reaction products.

Finally, the reaction course is affected by the nature of the halogen in the halide radical. Since halogens bring about an increase in the statistical effect of conjugation in the order: I > Br > Cl > F, an acid bromide will react with an organomagnesium compound more energetically than a chloride.

Di-ortho-substituted aryl magnesium halides react with acid bromides again with formation exclusively of ketones, but the yield of the latter is considerably higher.

It is more difficult to stop the reaction between mono-ortho-substituted aryl magnesium bromides and acid bromides at the first stage than it is with acid chlorides. Whereas with the latter the preparation of ketones is entirely feasible, with the acid bromides the formation of ketones under the same conditions is accompanied by formation of tertiary alcohol (or, more correctly, of their dehydration products in the shape of unsaturated hydrocarbons). Comparative results of reactions of aryl magnesium bromides with acetyl chloride and acetyl bromide are set out in Table 3.

TABLE 3

No.	Reactants	Ratio	Ketone	% yield of ketone	% yield of unsat. hydrocarbons
1	Mesityl magnesium bromide + acetyl chloride	1:1	Methyl mesityl ketone	10	–
2	Mesityl magnesium bromide + acetyl bromide	1:1	Methyl mesityl ketone	26	–
3	Mesityl magnesium bromide + acetyl bromide	2:1	Methyl mesityl ketone	51.5	–
4	o-Tolyl magnesium bromide + acetyl chloride	1:1	Methyl-o-tolyl ketone	30	14
5	o-Tolyl magnesium bromide +acetyl bromide	1:1	Methyl-o-tolyl ketone	20	19
6	α-Naphthyl magnesium bromide + acetyl chloride	1:1	Methyl α-naphthyl ketone	50	2.5
7	α-Naphthyl magnesium bromide + acetyl bromide	1:1	Methyl α-naphthyl ketone	34	10
8	Phenyl magnesium bromide + acetyl chloride	1:1	Methyl phenyl ketone	19	22
9	Phenyl magnesium bromide + acetyl bromide	1:1	Methyl phenyl ketone	17	39

Bromides of monocarboxylic acids can therefore be utilized for preparation of ketones with maintenance of the specified reaction conditions only if the second component is a di-ortho-substituted aryl magnesium halide.

The method of ketone synthesis here developed, based on reaction of acid chlorides with organomagnesium compounds, is highly suitable for the preparation of those carbonyl-containing compounds which are not synthesized by the Gustavson reaction (reaction of hydrocarbons with acid chlorides in presence of anhydrous aluminium chloride) due to the ease of modification of one of the reaction components under the influence of the catalyst. The new synthesis is illustrated by the reaction between camphane carboxylic acid chloride and α-naphthyl magnesium bromide. This reaction yielded bornyl α-naphthyl ketone in an amount corresponding to 66% of the theoretical.

EXPERIMENTAL

The following are the general conditions under which the reaction between organomagnesium compounds and acid halides is performed.

To the acid halide, dissolved in three times the volume of ether and placed in an ice water-cooled flask, is added an ethereal solution of the organomagnesium compound. This order of mixing is suitable both for mono-substituted aryl magnesium bromides and for aryl magnesium bromides not substituted in the ortho-position; however, when mixing the latter class with the ether solution of acid chloride the cooling should be intensified (using snow + salt). In the case of di-ortho-substituted aryl magnesium bromides, the reverse (usual) order of mixing with the acid halides is permissible.

After mixing, the mixture is heated for 6 hours. Although the heating period may be cut down for mono-ortho-substituted and unsubstituted aryl magnesium bromides, the 6-hour period was maintained in all the experiments in order to obtain comparable results. At the end of the heating period addition was made to the reaction mixture of an approximately equal volume of water and heating continued for one hour to permit saponification of the residual acid chloride. Addition was then made of a little dilute acetic acid (sufficient to clarify the ether

solution), the aqueous layer is separated, and the remaining ether layer washed with 10% soda solution and then with water until neutral. The ether solution is dried with anhydrous sodium sulfate and the ether driven off. The reaction products are then distilled in vacuum and analyzed. Results are detailed in Tables 1, 2 and 3.

Synthesis was also effected under the above conditions of bornyl α-naphthyl ketone.

Synthesis of bornyl α-naphthyl ketone. The reactants were 27 g (0.125 mole) naphthyl bromide, 4 g magnesium and 24 g (0.125 mole) camphane carboxylic acid chloride. The main fraction (210-220° at 7 mm) amounted to 28.0 g. The residue in the flask weighed 1 g. A second distillation of the main fraction gave 24.0 g boiling at 218-219° (7 mm) or 66 % of theory. The substance rapidly crystallized and after 3 recrystallizations from petroleum ether had the constant m. pt. of 109-110° (bornyl α-naphthyl ketone). This ketone has not been described in the literature.

0.1564 g substance: 0.4939 g CO_2; 0.1250 g H_2O. Found %: C 86.17; H 8.30. $C_{21}H_{24}O$. Calculated %: C 86.26; H 8.26.

To one part of the ketone dissolved in glacial acetic acid was added a slight excess of phenylhydrazine. After standing for 10 hours the crystalline phenylhydrazone of bornyl α-naphthyl ketone had separated. M. pt. 128° from toluene).

0.1244 g substance: 7.8 ml N_2 (20°, 760 mm). Found %: N 7.33. $C_{27}H_{30}N_2$. Calculated %: N 7.31.

Another portion of the ketone was reduced (Clemenson reaction) to a hydrocarbon – bornyl α-naphthyl methane. B. pt. 239° (14 mm), m. pt. 104° (from petroleum ether).

0.1952 g substance: 0.6474 g CO_2; 0.1652 g H_2O. Found %: C 90.51; H 9.47. $C_{21}H_{26}$. Calculated %: C 90.59; H 9.41.

SUMMARY

1. By means of a much larger amount of experimental material, confirmation was obtained of previous conclusions regarding the possibility of preparing ketones as the sole products of reaction of ortho-substituted aryl magnesium halides with monocarboxylic acid halides.

2. It was established that the quantitative yield of ketones is markedly affected by the character of the radical and by the character of the halogen entering into the composition of the acid chloride.

3. It was also shown that the method of synthesis which was developed is very suitable for the preparation of those carbonyl-containing compounds which cannot be synthesized by the Gustavson reduction due to the ease of modification of one of the reactants in presence of the catalyst.

4. Three compounds not known in the literature are described: Bornyl α-naphthyl methane, bornyl α-naphthyl ketone and its phenylhydrazone.

LITERATURE CITED

[1] I. I. Lapkin and A. V. Lyubimova, J. Gen. Chem., 19, 707 (1949).*

[2] M. Kharasch and Flenner, J. Am. Chem. Soc., 54, 674 (1922).

[3] See C. D. Hurd, Pyrolysis of Carbon Compounds, p. 30 (1938).

Received June 17, 1952

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* See Consultants Bureau translation, p. 677.

ADDITION OF DIALKYL PHOSPHOROUS ACIDS TO UNSATURATED COMPOUNDS

VII. ADDITION OF DIALKYL PHOSPHOROUS ACIDS TO α,β-UNSATURATED KETONES OF THE ALIPHATIC SERIES

A. N. Pudovik

In a series of previous papers we have shown that in presence of alkali metal alcoholates the dialkyl phosphorous acids add on extremely energetically and rapidly to α,β-unsaturated ketones with formation of esters of β-ketophosphonic acids. Yields of 60-75 % were obtained of the products of addition of dialkyl phosphorous acids to β,β-dimethyldivinyl ketone, ethylideneacetone, benzylidene acetone and furfurylidene acetone [1]. Using β,β-dimethyldivinyl ketone as an example, it was shown that when using equimolar amounts of acid and ketone the addition takes place only at the unsubstituted vinyl group, and, in accordance with the general principles of electronic theory, it proceeds in such a manner that the negatively polarized phosphonium group adds on to the positively polarized β-carbon atom of the vinyl group:

A similar order of addition, as we previously demonstrated, is observed also in all other cases of addition of dialkyl phosphorous acids to α,β-unsaturated electrophilic reagents: Unsaturated nitriles [2], aldehydes and esters of carboxylic acids [3].

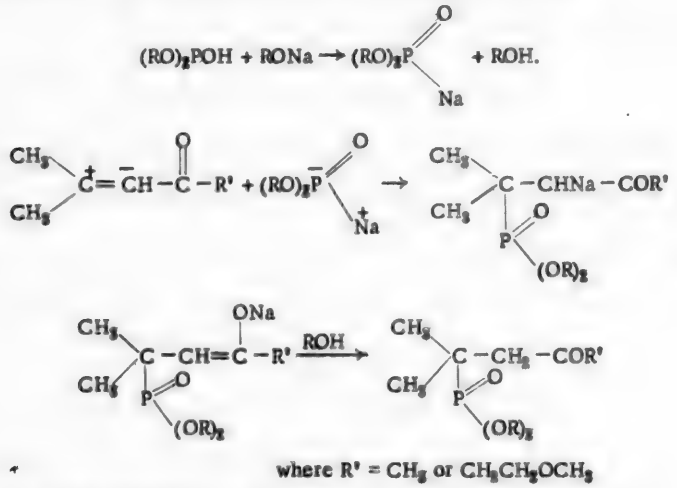
In a study of the addition of dialkyl phosphorous acids to β-substituted vinyl ketones it was also noted that the presence of substituted groups, especially phenyl, reduce in large measure the velocity of the addition reaction in comparison with the unsubstituted vinyl group of dimethyldivinyl ketone. This observation may be explained by the reduction of the electrophilic character of β-carbon atom by the presence of substituents which possibly create certain steric hindrances in addition.

In continuing and developing the investigation started by us, it appeared of interest to study the addition of dialkyl phosphorous acids to monovinyl ketones with a still larger number of substituents on the vinyl group and to elucidate the influence of their nature, distribution and number on the speed and order of the addition. From this aspect we instituted experiments on the addition of dialkyl phosphorous acids to mesityl oxide, β,β-dimethylvinyl-β'-methoxyethyl ketone, α,β-dimethylvinyl methyl ketone , and α-methylvinyl-γ-methoxypropyl ketone.

In the first instance we performed experiments with mesityl oxide and β,β-dimethylvinyl-β'-methoxyethyl ketone, each with two methyl groups at the β-carbon atom. In order to avoid radical exchange between the molecules of dialkyl phosphorous acids and the alcoholates used as catalysts, and in order also to ensure maximum purity of the resultant addition products, the alcoholates were prepared from alcohols with the same radicals as entered into the composition of the dialkyl phosphorous acids.

It may be suggested that the presence of two methyl groups on the β-carbon atom of the vinyl group may so reduce its electrophilic character and modify its spatial characteristics that more favorable conditions will be created for addition of dialkyl phosphorous acids not at the double bond but at the carbonyl group. In fact, it was observed that addition in the case of both of the ketones proceeds much less energetically in comparison with ketones containing an unsubstituted vinyl group or one substituent at the β-carbon atom, and requires for its completion rather large amounts of a saturated alcoholic solution of the alcoholate (up to several milliliters). With mesityl oxide the yields of addition products were of the order of 68-78%; with β,β-dimethyl-β'-methoxyethyl ketone they were very low; the main bulk of reaction mixture was converted during distillation into a nearly solid vitreous mass; in the pure form the only addition product isolated was diethyl phosphorous acid. For the purpose of determining the structure of the prepared addition products we first chose Tserevitinov's method as being simpler and more convenient (determination of the presence of hydroxyl groups). It was found that at room temperature the addition products

react with methyl magnesium iodide only very slowly and incompletely; on heating, the reaction proceeds rapidly and the hydroxyl group can be determined with little error. On this basis we arrived at the preliminary conclusion that the prepared addition products can be regarded as unsaturated hydroxyphosphonic esters [4]. A more detailed study of the properties of the products, however, did not confirm this assumption. It was found that these products do not add on bromine and were not oxidized by potassium permanganate; on acting with phenylhydrazine upon the products of addition of diethyl phosphorous acid to mesityl oxide, a phenylhydrazone was obtained in 69% yield. These results led us to the conclusion that the addition products are not unsaturated α-hydroxyphosphonic esters but esters of β-ketophosphonic acids. The reaction proceeds according to the scheme:



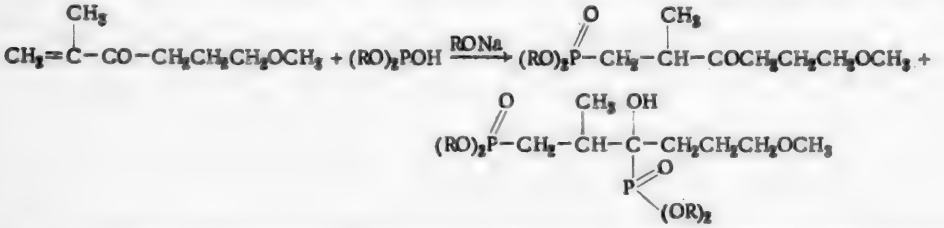
where R' = CH_3 or $CH_3CH_2OCH_3$

The constants, yields, and analytical data are set forth in Table 1. *

The results of quantitative determinations of hydroxyl groups** in the prepared esters of β-ketophosphonic acids by the Tserevitinov method are undoubtedly due to enolization of the carbonyl groups which proceeds slowly at room temperature but rapidly on heating.

We also obtained analogous results when investigating the addition of dialkylphosphorous acids to α,β-dimethylvinyl ketone. The addition products likewise do not add on bromine and are not oxidized by permanganate. The phenylhydrazone prepared from the ketone-diethyl phosphorous acid addition product was a very viscous oil which decomposed with evolution of a large amount of very volatile substances when an attempt was made to distill it in a vacuum (1 mm). The constants and yields of the prepared 3-methyl-4-dialkylphosphopentanones-2 are presented in Table 2.

Slightly different results were obtained in the addition reaction of dialkyl phosphorous acids and α-methylvinyl-γ-methoxypropyl ketone synthesized by the method of Nazarov and Zaretskaya [5]. Addition to this ketone of dimethyl phosphorous acid and diethyl phosphorous acid resulted in each case in the formation of two products: a low-boiling product of addition of one molecule of dialkyl phosphorous acid, and a high-boiling product of addition of two molecules of dialkyl phosphorous acid. In the second case the addition clearly proceeds both at the double bond and at the carbonyl group; part of the unreacted unsaturated ketone is recovered unchanged on distillation:



Accurate determination of the hydroxyl groups in the prepared esters of hydroxydiphosphinic acids proved impossible due to their poor solubility in the dibutyl and diisoamyl ethers used as solvents.

* All the experiments were performed with heating of the reaction mixture at 90-95° for 30-60 minutes with occasional stirring.

** Hydroxyl group determinations were made at 90-95°.

TABLE 1

No.	Formula	Boiling point	n_D^{20}	d_4^{20}	Phosphorus content (%) Found	Phosphorus content (%) Calcd.	Hydroxyl group content (%) Found	Hydroxyl group content (%) Calcd.	Yield (%)
1	$(CH_3O)_2P(=O)-C(CH_3)_2-CH_2COCH_3$	136° (12 mm)	1.4457	1.1163	14.9	15.3	–	–	70.3
2	$(C_2H_5O)_2P(=O)-C(CH_3)_2CH_2COCH_3$	138 (11 mm)	1.4400	1.0675	13.4	13.1	7.7	7.2	78.6
3	$(iso\text{-}C_4H_9O)_2P(=O)-C(CH_3)_2CH_2COCH_3$	162-163 (12 mm)	1.4409	1.0029	10.8	10.6	6.2	5.8	68.7
4	$(n\text{-}C_4H_9O)_2P(=O)-C(CH_3)_2CH_2COCH_3$	171-172 (13 mm)	1.4440	1.0084	10.5	10.6	–	–	77.2
5	$(C_2H_5O)_2P(=O)-C(CH_3)_2CH_2-CO-CH_2CH_2OCH_3$	164-168 (10 mm)	1.4500	1.1129	13.5	13.1	6.7	6.1	12

TABLE 2

No.	Formula	Boiling point	n_D^{20}	d_4^{20}	Hydroxyl group content (%) Found	Hydroxyl group content (%) Calcd.	Yield (%)
1	$(CH_3O)_2P(=O)-CH(CH_3)-CH(CH_3)-CO-CH_3$	136-137° (11 mm)	1.4475	1.1159	8.1	8.1	50.4
2	$(C_2H_5O)_2P(=O)-CH(CH_3)-CH(CH_3)-CO-CH_3$	158° (20 mm)	1.4390	1.0442	7.7	7.2	66.3

As we pointed out in a previous paper [2] the addition of a second molecule of dialkyl phosphorous acids to the carbonyl groups proceeds also with all the other ketophosphonic acids which we had previously prepared, but only after completion of the addition of the first molecule of dialkyl phosphorous acid at the double bond of the unsaturated ketone.

Saponification of the esters of β-ketophosphonic acids in the presence of dilute hydrochloric acid yielded the β-ketophosphonic acids themselves in the form of viscous, straw-colored liquids. Also prepared and analyzed was the acid barium salt of 4-methyl-4-phosphopentanone-2, a white powder.

EXPERIMENTAL

Addition of dialkyl phosphorous acids to mesityl oxide and β,β-dimethyl-β'-methoxy-ethyl ketone. The addition was performed by the following general method: to a mixture of equimolar amounts of ketone and dialkyl phosphorous acid was added dropwise an alcoholic solution of sodium alcoholate. The alcoholic solution of sodium alcoholate was prepared with an alcohol containing the same radical as that entering into the composition of the dialkyl phosphorous acid. Increasing molecular weight of the dialkyl phosphorous acids was accompanied by a marked fall in the velocity of the addition reaction. After addition of the amount of alcoholate required for completion of the addition reaction, the reaction mixture was allowed to stand for 20-30 minutes and, after cooling, it was then distilled in vacuum from a small Arbuzov flask. The constants, yields, and analyses of the obtained products are set forth in Table 1.

Investigation of the properties of 4-methyl-4-diethylphosphotentanone-2. 1. Action of bromine. The determination was performed by the McIlhiney method in chloroform solution. Estimation was made of the bromine consumed on addition and substitution. The series of experiments led to the conclusion that substantially no addition occurs, when the sample is dissolved in bromine-in-chloroform, during the first 10-50 minutes and that substitution takes place but only to an insignificant degree. Beginning, however, at a certain instant, calculated at $1\frac{1}{2}$-2

hours from the start of the experiment, the bromine solution is almost instantaneously decolorized, signalizing a rapid substitution reaction. Supplementary amounts of bromine added to the reaction mixture after this moment were also very rapidly consumed by substitution.

2. Oxidation by potassium permanganate. 4.8 g of product was dissolved in 200 ml of water, followed by about 1 g of potassium permanganate (one-seventh of the theoretically required quantity). Even after standing for 5 days at room temperature, there was no decolorization or formation of manganese dioxide precipitate.

3. Preparation of the phenylhydrazone. Into a porcelain beaker were weighed 5 g ketone and 3 g phenylhydrazine, after which 10 ml absolute ethyl alcohol was run in. The solution was kept in a desiccator for 3 days at room temperature and then heated on the boiling water bath for 4 hours. No crystallization was observed even after cooling followed by prolonged standing at 0°. Vacuum distillation of the reaction mixture yielded 4.7 g of the phenylhydrazone of 4-methyl-4-diethylphosphopentanone-2 with b.p. 202-203° (4 mm) in the form of a very viscous, oily liquid with a light-brown color.

0.1624 g substance: 32.3 ml NaOH (T 0.017841). Found %: P 9.8. $C_{19}H_{31}O_3PN_2$. Calculated %: P 9.5.

4. Saponification with hydrochloric acid. 3.6 g product with 60 ml dilute hydrochloric acid (1:1) were heated in a sealed tube at 130-140° for 9 hours. A total of 1.6 g ethyl chloride was formed (the theoretical requirement is 1.8 g). Following evaporation of the reaction mixture for many hours with periodic addition of distilled water, the whole of the hydrochloric acid was driven off. Evaporation of the aqueous solution yielded the ketophosphonic acid in the form of a straw-colored viscous liquid. Even after prolonged standing the acid did not crystallize. The barium salt (a white powder) was prepared from it.

0.0344 g substance: 0.4505 g $BaSO_4$. Found %: Ba 28.3. $C_{10}H_{20}O_6P_2Ba$. Calculated %: BA 27.7.

Addition of dimethyl phosphorous acid to α,β-dimethylvinylmethyl ketone. To a mixture of 9.8 g ketone and 11 g dimethyl phosphorous acid was added dropwise a saturated solution of sodium methylate in methyl alcohol. The reaction only started after 10-15 drops of methylate had been added, and proceeded with considerable heat evolution with continued addition. Distillation of the reaction mixture gave 14.1 g of 3-methyl-4-dimethylphosphopentanone-2:

B.p. 136-137° (11 mm); n_D^{20} 1.4475; d_4^{20} 1.1159.

0.1686 g, 0.1364 g substance: 50.7 ml, 41.4 ml NaOH (T 0.017841)
Found %: P 14.9, 15.0. $C_8H_{17}O_4P$. Calculated %: P 14.9.

Examination of the product showed that it did not add on bromine (only substitution occurred) and was not oxidized by permanganate. With phenylhydrazine it gave a phenylhydrazone in the form of a very viscous, brown oil. An attempt to fractionate the phenylhydrazone in vacuum (1 mm) was accompanied by violent decomposition with evolution of a large quantity of white fumes and of low-boiling products which condensed in the condenser. Saponification of the phosphonic ester gave the ketophosphonic acid in the form of a thick, straw-colored liquid.

Addition of diethyl phosphorous acid to α,β-dimethylvinyl methyl ketone. To a mixture of 4 g ketone and 5.5 g diethylphosphorous acid was added dropwise a saturated solution of sodium ethylate in ethyl alcohol. After termination of the reaction and cooling, the mixture was fractionated from a small Arbuzov flask, giving 6.3 g of 3-methyl-4-diethylphosphopentanone-2.

B.p. 158° (20 mm); n_D^{20} 1.4390; d_4^{20} 1.0442.

0.1626 g substance: 41.7 ml NaOH (T 0.017841). Found %: P 12.7. $C_{10}H_{21}O_4P$. Calculated %: P 13.1.

Addition of dimethyl phosphorous acid to α-methylvinyl-γ-methoxypropyl ketone. 11 g of α-methylvinyl-γ-methoxypropyl ketone (b.p. 60-62° (10 mm); n_D^{20} 1.4430) was reacted with 14.2 g dimethyl phosphorous acid, using sodium methylate solution as catalyst. Addition of the methylate to the reaction mixture led to considerable heating. After the reaction had been cooled and allowed to stand at room temperature for an hour, it was distilled in vacuum to give two substances: a) 1-Dimethylphosphone-2-methyl-6-methoxyhexanone-3 (2.1 g):

B.p. 161-164° (11 mm) n_D^{20} 1.4656; d_4^{20} 1.1098.

0.1470 g, 0.2018 g substance: 38.0 ml, 52.1 ml NaOH (T 0.01768).
Found %: P 12.6, 12.6. $C_{10}H_{21}O_5P$. Calculated %: P 12.3.

b) 1,3-Di-(dimethylphosphone)-2-methyl-6-methoxyhexanol-3 (5.1 g):

B.p. 236-238° (16 mm); n_D^{20} 1.4840; d_4^{20} 1.2055.

0.1298 g, 0.1178 g substance: 45.4 ml; 41.1 ml NaOH (T 0.01768). Found %: P 17.1, 17.1. $C_{12}H_{25}O_6P_3$. Calculated %: P 17.1.

Addition of diethyl phosphorous acid to α-methylvinyl-γ-methoxypropyl ketone. To a mixture of 12 g of the ketone and 11.6 g of the acid was added, dropwise, a saturated solution of sodium ethylate in ethyl alcohol. The following substances were isolated after the reaction and distillation:

a) 1-Diethylphosphone-2-methyl-6-methoxyhexanone-3 (4.7 g):

B.p. 167-168° (12 mm); n_D^{20} 1.4620; d_4^{20} 1.0590.

Found %: P 10.98, 10.96. $C_{12}H_{25}O_5P$. Calculated %: P 11.06.

b) 1.3-Di-(diethylphosphone)-2-methyl-6-methoxyhexanol-3 (5.3 g):

B.p. 226-227° (12 mm); n_D^{20} 1.4769; d_4^{20} 1.1214.

0.1638 g substance: 50.2 ml NaOH (T 0.01768). Found %: P 15.0 $C_{16}H_{36}O_8P_2$. Calculated %: P 14.8.

SUMMARY

1. A study was made of the addition of dialkyl phosphorous acids to mesityl oxide, β,β-dimethylvinyl-β'-methoxyethyl ketone, α,β-dimethylvinyl methyl ketone and α-methylvinyl-γ-methoxypropyl ketone. In all cases addition takes place at the double bond with formation of the corresponding esters of ketophosphonic acids. In the case of α-methylvinyl-γ-methoxypropyl ketone, products of addition of two molecules of the dialkyl phosphorous acids are also obtained: addition proceeds both at the double bond and at the carbonyl group.

2. The presence of two methyl groups at the α- and β-carbon atoms, and particularly at the β-carbon atom, of the vinyl group of the unsaturated ketones sharply reduces the speed of addition of dialkyl phosphorous acids to them.

LITERATURE CITED

[1] A. N. Pudovik, J. Gen. Chem. 22, 462, 467 (1952); see Consultants Bureau translation, pp. 525, 531.

[2] A. N. Pudovik and B. A. Arbuzov, Proc. Acad. Sci. USSR 73, 327 (1950).

[3] A. N. Pudovik, J. Gen. Chem. 22, 473 (1952); see Consultants Bureau translation, p. 537.

[4] A. N. Pudovik, Proc. Acad. Sci. USSR 73, 499 (1950).

[5] I. N. Nazarov and I. I. Zaretskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 1, 211 (1941).

Received November 25, 1950

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ALLYL REARRANGEMENTS

XVI. FORMATION OF ACETATES AND ALCOHOLS FROM BUTOXYCHLOROPENTENES

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In a series of previous papers we have described the saponification reactions of isomeric methoxychloropentenes [1] and dichlorobutenes [2] and the preparation from them of acetates by the action of sodium acetate. It was shown that two mechanisms are involved: Bimolecular nucleophilic substitution leading to products without rearrangement; and a monomolecular mechanism yielding carbonium ions and leading to identical mixtures of products of both of the isomeric chlorides. Primary haloallyl isomers react predominantly according to the bimolecular mechanism in the reactions of saponification and of ester formation, while secondary compounds react according to the monomolecular mechanism.

The purpose of the present investigation was the further study of the saponification reactions and of the formation of acetates from haloallyl compounds with reference to the reactions of the primary and secondary butoxychloropentenes, and the elucidation of the effect of the $C_4H_9OCH_2CH_2$ radical in them upon the ratio of the substitution reactions. On acting with potassium acetate upon 1-butoxy-5-chloro-3-pentene in acetic acid solution, we obtained a mixture of acetates consisting of 93% of 1-butoxy-3-penten-5-yl acetate and 7% of 1-butoxy-4-penten-3-yl acetate. The total yield of acetates was 81%. An experiment under analogous conditions with 1-butoxy-3-chloropentene-4 gave a mixture of 59% of 1-butoxy-3-penten-5-yl acetate and 41% of 1-butoxy-4-penten-3-yl acetate. The acetates are stable and show little tendency to change either under thermal isomerization conditions (100°) or on heating in acetic acid solution, i.e. under conditions similar to those used in their preparation.

When our paper was completed a paper appeared by Emerson, Dubel and Longley [3] which describes the preparation of a series of alkoxychloropentenes, a large number of which had previously been prepared and described by us [4], likewise the reactions of some of them. They gave details, in particular, of the reaction of 1-butoxy-5-chloro-3-pentene with sodium acetate in acetic acid solution, but they only succeeded in isolating one product — 1-butoxy-3-penten-5-yl acetate in 77% yield, whose constants were identical with those of our own preparation. In general they did not study the reaction with the secondary chloride.

The saponification of both of the isomeric acetates of butoxypentenols, under our conditions, proceeds without isomerization, thus providing an additional proof of the fact that saponification of esters of alcohols of the allyl type proceeds without rupture of the alcoholic carbon-oxygen bond, and consequently, without formation of the carbonium ion. We effected the saponification of the isomeric butoxychloropentenes with aqueous sodium carbonate. Saponification of 1-butoxy-5-chloro-3-pentene gave a mixture of alcohols consisting of 79% 1-butoxy-3-penten-5-ol and 20.3% 1-butoxy-4-penten-3-ol, while the mixture obtained from 1-butoxy-3-chloro-4-pentene comprised 56.6% 1-butoxy-3-penten-5-ol and 43% 1-butoxy-4-penten-3-ol. The results in the present investigation are very similar to those in the preceding papers [1,2]. In analogy with the earlier investigations, we may conclude that saponification of secondary butoxychloropentene and its reaction with alkali metal acetates proceed mainly according to a monomolecular mechanism, while the primary compound reacts according to a mixed mono- and bimolecular mechanism. On the basis of the present results we may also conclude that substitution of the radical $CH_3OCH_2CH_2$ for $C_4H_9OCH_2CH_2$ in the haloallyl system has very little influence upon the relative extents of the substitution reactions of the halide with the hydroxyl and acetate groups, which proceed according to the bimolecular and monomolecular mechanisms.

EXPERIMENTAL

Action of potassium acetate on 1-butoxy-5-chloro-3-pentene in acetic acid solution. 39.5 g 1-butoxy-5-chloro-3-pentene, 23 g glacial acetic acid and 30 g calcined potassium acetate were heated for 27 hours at a bath temperature of 140-150°. After cooling, the reaction mixture was treated with water and then with soda solution prior to extraction with ether. The ether extract was dried with calcium chloride, the ether

driven off, and the residue distilled in vacuum, using a spiral column. 2.5 g 1-butoxyl-4-penten-3-yl acetate was obtained.

B.p. 99-100° at 9 mm; n_D^{20} 1.4298; d_4^{20} 0.9240; MR_D 55.89; calculated 55.71.

0.1204 g substance: 0.2908 g CO_2; 0.1048 g H_2O. Found %: C 65.91; H 10.2. $C_{11}H_{20}O_3$. Calculated %: C 66.00; H 10.00,

There was also obtained 34 g 1-butoxy-3-penten-5-yl acetate:

B.p. 116-117° at 9 mm; n_D^{20} 1.4390; d_4^{20} 0.9399; MR_D 55.97; calculated 55.71.

0.0975 g substance: 0.2353 g CO_2; 0.0856 g H_2O. Found %: C 65.86; H 9.82. $C_{11}H_{20}O_3$. Calculated %: C 66.00; H 10.00.

Addition of bromine to 1-butoxy-3-penten-5-yl acetate gave the dibromide:

B.p. 173-175° at 17 mm; n_D^{20} 1.4840; d_4^{20} 1.4267; MR_D 72.10; calculated 71.75.

0.1298 g substance: 0.1345 g AgBr. Found %: Br 44.06. $C_{11}H_{20}O_3Br_2$. Calculated %: Br 44.38.

Action of potassium acetate on 1-butoxy-3-chloro-4-pentene in acetic acid solution. 39.5 g 1-butoxy-3-chloro-4-pentene, 23 g glacial acetic acid and 30 g powdered anhydrous potassium acetate were heated at a bath temperature of 130-140° for 46 hours. Treatment of the reaction mixture was as above. Distillation of the products yielded 10.4 g 1-butoxy-4-penten-4-yl-acetate:

B.p. 98.5-99° at 8.5 mm; n_D^{20} 1.4300; d_4^{20} 0.9240,

and 14.9 g 1-butoxy-3-penten-5-yl acetate:

B.p. 115-116° at 8.5 mm; n_D^{20} 1.4390; d_4^{20} 0.9399.

The dibromide was obtained by reacting bromine with 1-butoxy-4-penten-3-yl acetate:

B.p. 162-164° at 12 mm; n_D^{20} 1.4810; d_4^{20} 1.4230; MR_D 71.92; calculated 71.75.

0.1134 g substance: 0.1181 g AgBr. Found %: Br 44.28. $C_{11}H_{20}O_3Br_2$. Calculated %: Br 44.38.

Experiments on determination of the stability of the isomeric pentenyl acetates.

Experiment 1. Glass ampoules containing respectively 1 g 1-butoxy-4-penten-3-yl acetate (n_D^{20} 1.4300) and 1 g 1-butoxy-3-penten-5-yl acetate (n_D^{20} 1.4390) were heated for 33 hours at 100°. No change in the refractive indices of the acetates was observed.

Experiment 2. Mixtures comprising 6 g acetic acid and 10 g, respectively, of 1-butoxy-4-penten-3-yl acetate and 1-butoxy-3-penten-5-yl acetate were heated for 33 hours at the temperature of the boiling water bath. Both isomers remained unchanged after the heating.

Saponification of 1-butoxy-3-penten-5-yl acetate. 6 g KOH was dissolved in 54 ml 96% alcohol, and to the solution was added 19.5 g 1-butoxy-3-penten-5-yl acetate. The mixture was heated on the water bath under a reflux condenser with mechanical stirring for 6 hours. After the alcohol had been driven off, the residue was treated with soda and extracted with ether. Fractionation of the residue after removal of the ether gave 10.6 g 1-butoxy-3-penten-5-ol:

B.p. 113-114° at 9 mm; n_D^{20} 1.4508; d_4^{20} 0.9115; MR_D 46.65; calculated 46.46.

0.1148 g substance: 0.2873 g CO_2; 0.0929 g H_2O. Found %: C 68.30; H 11.40; $C_9H_{18}O_2$. Calculated %: C 68.35; H 11.39.

Treatment of this alcohol with bromine gave the dibromide:

B.p. 157-158° at 7 mm; n_D^{20} 1.5071; d_4^{20} 1.5161; MR_D 62.35; calculated 62.38.

0.1254 g substance: 0.1480 g AgBr. Found %: Br 50.18. $C_9H_{18}O_2Br_2$. Calculated %: Br 50.25.

Saponification of 1-butoxy-4-penten-3-yl acetate. 3.6 g KOH was dissolved in 33 ml 96% alcohol, and to the solution was added 12 g 1-butoxy-4-penten-3-yl acetate. The mixture was heated on the water bath for 8 hours. The reaction mixture was worked up and distilled to give 7.2 g 1-butoxy-4-penten-3-ol:

B.p. 91-92° at 9 mm; n_D^{20} 1.4404; d_4^{20} 0.8995; MR_D 46.34; calculated 46.46.

0.1113 g substance: 0.2781 g CO_2; 0.1116 g H_2O. Found %: C 68.19; H 11.22. $C_9H_{18}O_2$. Calculated %: C 68.35; H 11.39.

Treatment with bromine gave the dibromide:

B.p. 154-155° at 6 mm; n_D^{20} 1.5030; d_4^{20} 1.5124; MR_D 62.08; calculated 62.38.

0.1163 g substance: 0.1368 g AgBr. Found %: Br 50.01. $C_9H_{18}O_2Br_2$. Calculated %: Br 50.26.

SUMMARY

1. A study was made of the reaction of the isomeric butoxychloropentenes with potassium acetate and of their saponification with aqueous sodium carbonate solution.

2. It was shown that the hydrolysis and formation of acetates from primary butoxychloropentene take place according to a mixed mono- and bimolecular mechanism with the latter predominating. Similar reactions with secondary butoxychloropentene proceed mainly according to a monomolecular mechanism.

LITERATURE CITED

[1] A. N. Pudovik and B. A. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1945, 541.

[2] A. N. Pudovik, J. Gen. Chem. 19, 1179 (1949). *

[3] W. Emerson, G. Dubel and R. Longley, J. Org. Chem. 14, 696 (1949).

[4] A. N. Pudovik, V. I. Nikitina and S. Aigistova, J. Gen. Chem. 19, 279 (1949). **

Received May 30, 1950

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* See Consultants Bureau translation, p. 1173.

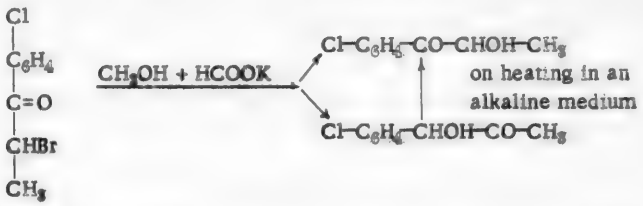
** See Consultants Bureau translation, p. 241.

MOLECULAR REARRANGEMENTS OF α-KETO ALCOHOLS

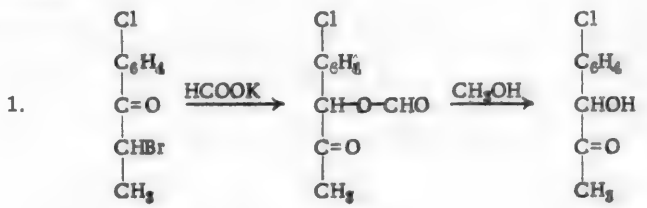
XI. MOLECULAR REARRANGEMENTS DURING METHANOLYSIS OF ESTERS OF α-KETO ALCOHOLS

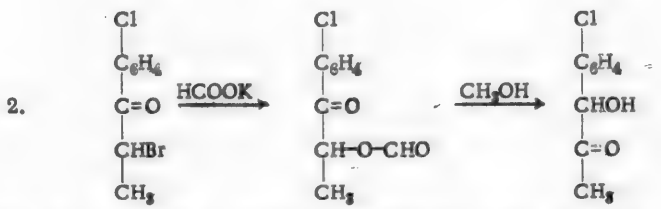
T. I. Temnikova and E. I. Kulachkova-Kmito

In previous investigations [1,2] it was shown that in the synthesis of some α-keto alcohols by the Klint method, the normal products of reaction are accompanied, as anticipated, by isomeric α-keto alcohols. The formation of a mixture of isomeric keto alcohols in this reaction was noted in a series of papers [3], but in all the previously studied examples the isomeric keto alcohols – the abnormal reaction products – were more stable, and their formation was explained by the isomerization of the primary normal reaction products. In the cases investigated by us the isomeric keto alcohols proved to be less stable and when heated under alkaline conditions they were transformed into the α-keto alcohols which are the normal reaction products:



In explanation of this phenomenon we put forward two possible mechanisms of the formation of the anomalous keto alcohol:





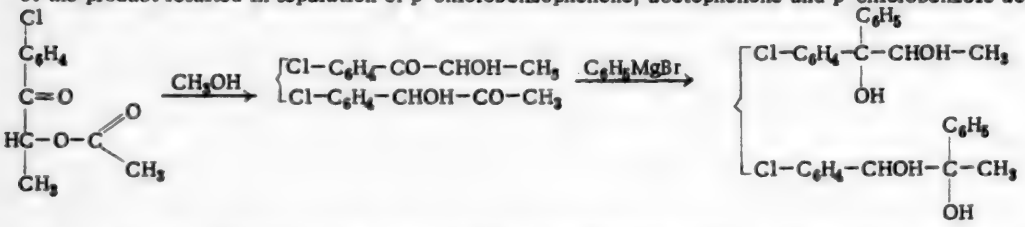
According to the first variant, molecular rearrangement takes place during the formation of the ester of the keto alcohol from the bromo ketone; this type of rearrangement has been described in the literature [4].

In the second case it is proposed that rearrangement occurs during the stage of methanolysis of the ester. Molecular rearrangements during methanolysis of esters of keto alcohols have not been described in the literature. On the basis of theoretical considerations we have considered the second variant to be more probable. The present investigation had the objective of throwing more light upon this stage.

Attempts to elucidate the process of separation of the formate of the keto alcohol and obtain evidence of its structure did not succeed. When the bromo ketone was reacted with potassium formate in a medium of 98% formic acid, the resultant product (distilled in vacuum) contained a considerable amount of the keto alcohol. Formation of the keto alcohol could proceed both through partial hydrolysis with water present in the reaction mixture and through decomposition of the formate during the distillation.

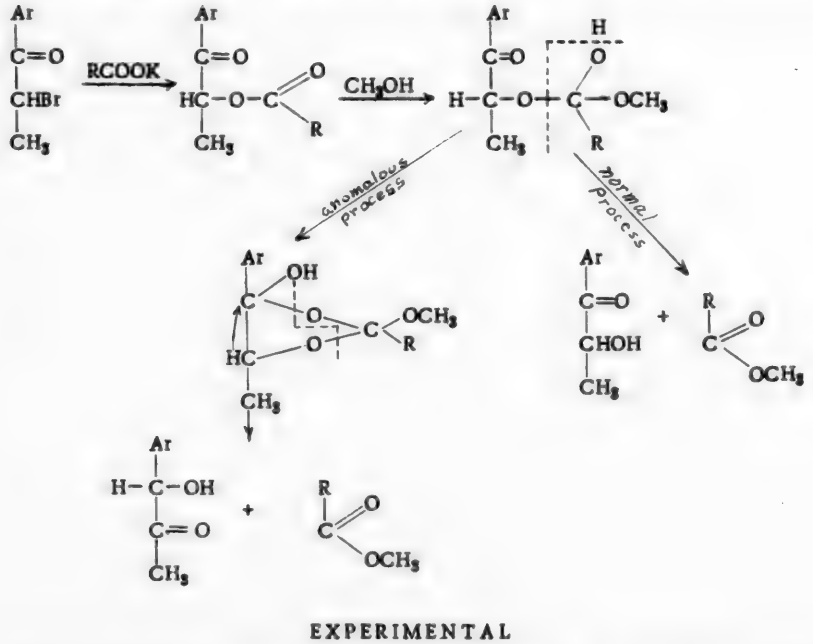
It was therefore impossible to obtain direct evidence of the rearrangement mechanism. In view of the failure to prepare the pure formate of the keto alcohol, experiments were performed to establish the possibility of extending the reaction to other esters or of effecting the methanolysis of the other esters of α-keto alcohols. In the present investigation we have studied the methanolysis of methyl-p-chlorobenzoyl carbinol acetate.

The acetate was prepared by the action of potassium acetate upon α-bromoethyl-p-chlorophenyl ketone and, as was shown in the previous communication, did not contain the isomeric acetate [2]. Heating of the ester on the boiling water bath with methyl alcohol for 20 hours in presence of sodium formate gave a mixture of keto alcohols in approximately the same ratio as was obtained in the methanolysis of the formic ester. Evidence of the presence of a mixture of keto alcohols was obtained by their conversion into glycols with the help of C_6H_5MgBr. Oxidation of the product resulted in separation of p-chlorobenzophenone, acetophenone and p-chlorobenzoic acid.



It has thus been established that the step of methanolysis of esters of keto alcohols may be complicated by a molecular rearrangement with formation of an isomeric keto alcohol not corresponding in structure to the initial bromo ketone.

The formation of an isomeric α-keto alcohol during methanolysis of esters of α-keto alcohols can be accounted for only by the occurrence in the complex, formed in the first stage of the process, of supplementary interaction between the carbonyl and hydroxyl groups to give a cyclic compound due to intramolecular addition. We may represent the course of the reaction by the following scheme:



EXPERIMENTAL

1. Action of sodium formate on α-bromoethyl-p-chlorophenyl ketone. 42 g α-bromoketone, 60 g anhydrous sodium formate and 100 ml formic acid (98%; d 1.2220) were heated for 30 hours at 100°. At the end of the reaction the formic acid was distilled off in vacuum and the residue distilled over at 134-137° (5 mm). Yield 6.2 g.

d_4^{20} 1.2457; n_D^{20} 1.5459; number of OH groups: 0.52, 0.52, 0.41.

2. Methanolysis of methyl-p-chlorobenzoyl carbinol acetate by methyl alcohol. Use was made of the ester prepared by the earlier described method [2]. It had b.p. 127-130° (1.5 mm); n_D^{16} 1.5332. 13 g of ester dissolved in 35 ml absolute methyl alcohol was heated on the boiling water bath with 10 g anhydrous sodium formate. At the conclusion of the reaction, the alcohol was distilled off in vacuum and the residue washed with water and extracted

with ether. The ether extract was dried with magnesium sulfate, the ether driven off, and the residue distilled in vacuum.

B.p. 112-114° at 1.5 mm; d_4^{15} 1.255; d_4^{20} 1.245; n_D^{16} 1.553; n_D^{20} 1.5498; MR_D found 47.04, calc. 46.564.

Yield 6 g of keto alcohol or 60% of theoretical. From 0.6 g was obtained 0.62 g semicarbazone with b.p. 176-178°.

Action of C_6H_5MgBr on the reaction product. To the C_6H_5MgBr obtained from 3.2 g Mg and 21 g bromobenzene while cooling with ice was added 5 g of reaction product. After the usual treatment [2] followed by removal of the ether, the material was dissolved in a large amount of ligroin from which spherical crystals separated. M.p. 88-90°. Yield 1.8 g.

0.0913 g substance: 0.2302 g CO_2; 0.0481 g H_2O. 0.0404 g substance: 0.1020 g CO_2; 0.0202 g H_2O. Found %: C 68.76, 68.85; H 5.89, 5.59. $C_{15}H_{15}O_2Cl$. Calculated %: C 68.58; H 5.71.

Oxidation of the reaction product. To 1.3 g substance was added 10 g lead tetraacetate in 20 ml glacial acetic acid and oxidation was performed at 55-65°. Further treatment was as before [2]. Steam-distillation yielded first an oil with the odor of acetophenone and then a solid which solidified in the condenser and melted, after drying, at 68-72°. A mixture with an authentic specimen of p-chlorobenzophenone (m.p. 72-74°) melted at 70-73°. The residue from the steam distillation was extracted with ether to give a crystalline, readily distillable compound with m.p. 233-235°. A mixture with p-chlorobenzoic acid had the same melting point.

The first part of the steam-distillate was oxidized with silver oxide for removal of aldehydes from the neutral oil and again steam-distilled. The distilled oil with a distinct odor of acetophenone was converted into the semicarbazone which, after several recrystallizations from alcohol, melted at 198-201°. A mixture with acetophenone semicarbazone also melted at 197-200°.

SUMMARY

1. Heating of methyl-p-chlorobenzoyl carbinol acetate with methyl alcohol in presence of sodium formate leads to methanolysis of the ester.

2. The methanolysis of methyl-p-chlorobenzoyl carbinol acetate is shown to be complicated by a molecular rearrangement which results in formation, side by side with the normal reaction product (methyl-p-chlorobenzoyl carbinol), of the isomeric keto alcohol — p-chlorophenylacetyl carbinol.

LITERATURE CITED

[1] T.I.Temnikova and L.A.Petrova. J.Gen.Chem., 21, 4 (1951); see Consultants Bureau translation, p. 745.

[2] T.I.Temnikova and E.I.Kulachkova. J.Gen.Chem., 19, 1324 (1949); C.B.trans., p. 1323.

[3] A.E.Favorsky and V.Vasilev. J.Russ.Chem.Soc., 60, 383 (1928); T.I.Temnikova. J.Gen.Chem., 10, 468 (1940).

[4] A.E.Favorsky. J.Russ.Chem.Soc., 60, 369 (1928); T.I.Temnikova. J.Gen.Chem., 8, 1022 (1938); T.I. Temnikova and V.I.Veksler. J.Gen.Chem., 19, 1318 (1949); see C.B.trans., p. 1315. V.I.Veksler. J.Gen.Chem., 20, 1285, 1289 (1950); see C.B.trans., pp. 1335, 1339.

Received December 14, 1950

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CHEMICAL REACTIONS AT EXTREMELY HIGH PRESSURES

I. REACTION OF BENZENE WITH ANHYDROUS ALUMINUM CHLORIDE

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Several authors have studied the action of anhydrous aluminum chloride on benzene: G. Gustavson [1] (1878 and later), Friedel and Crafts [2] (1882-1885), and others (see the survey of these investigations [3]). The reaction gives a complex mixture of hydrocarbons from which were isolated phenylcyclohexane, o-diphenylcyclohexane and 3-phenyl-1-methylcyclopentane. There are also indications of the presence in the reaction products of diphenyl, ethylbenzene, toluene and naphthalene (at higher temperatures). The yield of products was found to be most insignificant in spite of the experiments being prolonged for several weeks. For instance, in the experiments of Wertyporoch and Sagel [4] the total yield of products of reactions of benzene with aluminum chloride at 30° for 12 weeks was 8% of the weight of benzene.

No previous study has been reported on the effect of pressure on the reaction.

EXPERIMENTAL*

We performed experiments with anhydrous $AlCl_3$ and dry benzene (thiophene-free) taken in molar ratios of 0.8:1, using a stainless steel reactor at pressures up to 3300 atm. The reactor was fitted with a valve and pressure gage; heating was by an electric furnace covering the reactor. The temperature was kept constant within the limits of $\pm 2°$ with the help of a contact thermometer. Pressure was developed with a pump (up to 650 atm) and a hydraulic compressor; in experiments at pressures up to 1400 atm the reactor was first charged with the experimental mixture, and then benzene was pumped in to the required pressure with the pump or compressor. In experiments at pressures exceeding 1400 atm, the mixture was placed in a sealed lead ampoule and the pressure was developed with the help of a solution of water in glycerol which was pumped into the reactor with the hydraulic compressor. The reactor was heated for a period of 50-60 minutes; cooling was effected more slowly: in two hours after termination of heating the reactor had been cooled to 50°. The duration of an experiment (τ) was taken to be the period during which the reactor was at the specified temperature. After cooling and opening the reactor, its contents (or the contents of the lead ampoule) were poured onto ice; after the ice had melted, the product was extracted with ether, washed with water until neutral (removal of HCl), and dried over calcined sodium sulfate. The ether was then driven off, likewise the benzene (in a water bath) to a residual pressure of 20-25 mm). The liquid residue was weighed and fractionated in vacuum (1-2 mm) until the residue only contained resins which decomposed on further heating.

Variation of Yield of Products of Reaction with Pressure

In Tables 1 and 2 are presented the results of experiments on the reaction of benzene with anhydrous $AlCl_3$. The following conclusions can be drawn:

1) The total yield of reaction products increases with rising pressure.

2) Increase of pressure leads to a fall in the relative content of fractions boiling at lower temperatures (up to 140° at 1-2 mm).

These conclusions are generally applicable both for experiments performed directly in the reactor and for those in lead ampoules, notwithstanding the slight differences in the results of each of these series of experiments. These differences may have arisen from partial reaction of the released hydrogen chloride with the lead ampoule, resulting in formation of H_2 and $PbCl_2$. The amounts of lead chloride formed in Experiments 16 and 21 of the lead ampoule series were respectively 2.9 and 2.5 g.

*Mechanic V.A. Kuznetsov collaborated.

TABLE 1

Reaction of Benzene with $AlCl_3$ in a Stainless Steel Reactor at 100°

Expt. No.	C_6H_6 (g)	$AlCl_3$ (g)	τ (hrs)	P (atm)	Yield of products (wt.% of benzene)	Wt.% of fractions *			Notes
						up to 140°	140-170°	above 170°	
13	78.6	105.5	5	1 8 **	10.0	28.8	20.2	22.2	Fractionation to 215°
14	77.9	106.0	5	1.8 **	12.0	23.4	18.3	28.7	Fractionation to 213°
7	85.7	110.0	2	650	25.0	19.3	22.0 ****		
8	80.0	110.0	5	650	28.0	15.9	13.0	44.0	Fractionation to 240°
10	79.7	109.8	5	1400	24.0	6.8	9.6	62.0	Fractionation to 230°

TABLE 2

Reaction of Benzene with $AlCl_3$ in Lead Ampoules

Expt. No.	C_6H_6 (g)	$AlCl_3$ (g)	τ (hrs)	$t_\circ$	P (atm)	Yield of products (wt.% of benzene)	Wt.% of fractions *			Notes
							up to 140°	140-170°	above 170°	
21	44.9	59.9	5	100	1.8 **	10.2	17.0	17.2	29.4	Fractionation to 190°
16	45.0	60.5	2	100	2400	31.2	7.6	18.0	41.1	Fractionation to 243°
15 ***	9.24	11.0	2	120	3300	42.2				

* Fractionation at 1-2 mm mercury.

** Pressure of saturated benzene vapor at 100°.

*** Experiment carried out in a pressure apparatus.

**** Up to 180°.

Investigation of Composition of Reaction Products

The fractions obtained in Experiments 7 and 8 (Table 1), which were conducted at 100° and 650 atm, were subjected to two fractionations in succession at 1.2 mm. Only one crystalline substance was separated in this manner. We combined the crystals of this substance with those obtained in other experiments, separated them from oil with petroleum ether, filtered, and recrystallized them from benzene until the m.p. was constant.

The substance obtained is in the form of white needles with m.p. 156°, soluble in benzene, alcohol, and ether, and insoluble in water. Found %: C 93.62, 93.49; H 6.52, 6.58; M 209 (by Rast's method).

The composition, molecular weight and melting point correspond to those of 1,4-diphenyl-1,3-cyclopentadiene (m.p. 157-158°).

We prepared the picrate of this substance; m.p. (with decomposition) 145-146°, agreeing with that of the picrate of 1,4-diphenyl-1,3-cyclopentadiene [5].

Found %: C 51.30, 51.37, H 2.84, 3.02. $C_{29}H_{20}O_{14}N_6$. Calculated %: C 51.48; H 2.98.

Qualitative tests [5] were carried out (red solution with blue fluorescence in conc. sulfuric acid, yellow color of solution in mixture of chloroform and glacial acetic acid) and confirmed the identity of the substance with 1,4-diphenyl-1,3-cyclopentadiene.

The narrow fractions boiling below 180-190° (1.2 mm) were oily liquids whose viscosity increased with increasing boiling point; at temperatures above 190° an extremely viscous, dark-red oil came over and solidified to a vitreous mass in the receiver. Each of the fractions was analyzed for C and H and molecular weight (Rast), and the boiling points at atmospheric pressure were determined.

The first two fractions – 70-75° (1.2 mm) and 107-110° (1.2 mm) – were obtained in small quantities. Analyses of these fractions gave the following results:

1st Fraction 70-75° (1.2 mm). Found %: C 91.17, 90.87; H 9.05, 9.29.
2nd Fraction 107-110° (1.2 mm). Found %: C 91.91, 91.76; H 8.07, 8.16.

In Table 3 are set forth the results of examination of the higher boiling fractions together with the constants [6] of the assumed components of the mixture.

Examination of Table 3 indicates that Fraction 3 resembles diphenylcyclopentane whose presence was to be expected on the basis of examination of the crystalline product of the reaction (see Table, next page). In this fraction, however, there is also evidence of the presence of diphenylcyclohexane (and methyldiphenylcyclopentane). The constants of Fractions 5 and 6 are close to those of, respectively, triphenylcyclopentane and triphenylcyclohexane; Fraction 4 is apparently intermediate. Concerning Fractions 1 and 2 (see next page), they are evidently a

TABLE 3

Comparison of Results of Examination of Fractions with the Constants of the Assumed Components of the Mixture

Substance (or fraction)	B.p. (°)	C (%)	H (%)	M
Third fraction	300-306 (760)* 130-132 (1.2)	91.87, 91.88	8.36, 8.36	242
1,3-Diphenylcyclopentane	140-141 (3)	91.84	8.16	222
1,3-Diphenylcyclohexane	196-198 (17)			
1,4-Diphenylcyclohexane	190 (29)	91.53	8.47	236
Methyldiphenylcyclopentane	No data			
Fourth fraction	323-326 (760) 145-147 (1.2)	92.35, 92.25	7.92, 8.01	260, 268
Fifth fraction	330-340 (760) 165-170 (1.2)	92.93	7.34	287
1,2,4-Triphenylcyclopentane	285 (50)	92.62	7.38	298
Sixth fraction	360-380 (760) 190-200 (1.2)	92.24, 92.49	7.57, 7.69	308, 332
Triphenylcyclohexane. . . .	No data	92.32	7.68	312

*The pressure in mercury is given in brackets

mixture of phenylcyclohexane (or methylphenylcyclopentane) with the components of Fraction 3, although the composition of Fraction 2 is remarkably close to that of Fraction 3.

The experimental data thus justify the assumption that phenylated cyclohexanes and cyclopentanes are present in the reaction products.

DISCUSSION OF RESULTS

The foregoing data for the benzene–aluminum chloride interaction at pressures up to 3300 atm testify to the very great diversity of the reactions involved. These reactions evidently proceed within the complex constituted by the starting materials but may also involve hydrogen chloride. Without entering into speculation about the mechanism of the action of hydrogen chloride, we may point out that at the present time there is no doubt about the formation of a reactive complex in other similar reactions. Our data correlating the product yield with pressure show that the formation of the reactive complex and the sum total number of reactions taking place are accompanied by a reduction in volume. This was also to be expected because these reactions result in the formation of higher molecular hydrocarbons, and the hydrogen evolved during condensation is partly consumed in the hydrogenation of these hydrocarbons.

It must be noted that the increase of total yield of products with rising pressure is extremely significant (the increase is threefold with rise of pressure from 1.8 atm to 2400 atm). It is natural that the biggest increase in yield should apply to the hydrocarbons of highest molecular weight whose formation proceeds with maximum contraction in volume; this finds expression in our observation of the fall in the relative content of the lower boiling fractions in the reaction products.

SUMMARY

1. The effect of pressure up to 3300 atm on the interaction of benzene with anhydrous aluminum chloride has been investigated. Increase of pressure brings about a marked increase in the total yield of products and also increases the relative content of higher molecular products.

2. The products of interaction of benzene with anhydrous aluminum chloride under pressure were examined. Crystalline 1,4-diphenyl-1,3-cyclopentadiene was isolated and identified. The isolated liquid fractions resemble phenylated cyclohexanes and cyclopentanes in respect of chemical composition, boiling point and molecular weight.

LITERATURE CITED

[1] G.Gustavson. J.Russ.Chem.Soc., 10, 390 (1878); Comptes rend., 146, 640 (1908).

[2] C.Friedel and I.M.Crafts. Ber., 15, 1451 (1882).

[3] Thomas. Anhydrous Aluminum Chloride in Organic Chemistry. I-L Press (1949).

[4] E.Wertyporoch and H. Sagel. Ber., 66, 1306 (1933).

[5] N.L.Drake and I.R.Adams. J.Am.Chem.Soc., 61, 1326 (1939).

[6] G.Egloff. Physical Constants of Hydrocarbons (1947).

Received January 23, 1951

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CHEMICAL REACTIONS AT EXTREMELY HIGH PRESSURES

II. REACTION OF BENZENE WITH CARBON DIOXIDE

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In 1931 Kinney and Langlois reported [1] that they had succeeded in preparing a small quantity of benzoic acid (0.13% of the weight of starting benzene) by heating benzene with CO_2 for 10 hours at 300° and 35 atm in presence of a catalyst of the type of Zn-Cu-Cr oxides. Subsequently (in 1935), however, in a paper by Kinney and Bonner [2] these results were described as erroneous on the basis of the authors' thermodynamic calculation of the equilibrium in the reaction:

$$C_6H_6 + CO_2 \rightleftarrows C_6H_5COOH. \qquad (1)$$

They stated that at 25°, ΔF = 4300 cal/mole (log K = −3.1), while at 250° ΔF = 18170 cal/mole (log K = −7.6).

The reaction of formation of benzophenone is even less advantageous from the thermodynamic viewpoint. Thus, at 25° the ΔF of this reaction is about 7 kcal/mole, i.e. K is about 10^{-5}. We have performed an approximate calculation of the effect of pressure on the equilibrium constant of reaction (1).

Data for the compressibility of CO_2 at pressures up to 3000 atm in the temperature range of 0-150° are given by Michels and co-workers [3]. From these data Michels calculated in another paper [4] the free energy of carbon dioxide under pressure. Without going into the details of our own calculations, we may limit ourselves to saying that this calculation was based upon an extrapolation of Michels' data into the region of higher temperatures and pressures. One result of this procedure was that the isochores of carbon dioxide at 0-150° and at densities of 0.9-1.2 g/cm^3 were nearly rectilinear; this fact permitted easy extrapolation of P-V-T data at high pressures into the higher temperature region with the help of the formula:

$$P_T = P_{T_0} + a(T-T_0) \quad (\rho = \text{const.}).$$

The computations lead to the conclusion that at 300° and 5000 atm the equilibrium constant of the reaction of formation of benzoic acid from benzene and CO_2 is roughly 10^{-4}. Consequently the theoretical yield of benzoic acid even under super-high pressures is negligibly small.

On the other hand, Friedel and Crafts [5] long ago observed the formation of small amounts of benzoic acid after passing dry carbon dioxide through a mixture of benzene and anhydrous aluminum chloride heated nearly to boiling. At the same time a little hydrogen chloride was evolved. The authors suggested the formation of the compound $C_6H_5COOAl_2Cl_5$, which by reaction with water splits up to form benzoic acid.

In the patent literature [6] is described the preparation of benzoic acid by heating benzene with carbon dioxide in presence of anhydrous $AlCl_3$ (50% of the weight of the benzene) at 100° and 60 atm for 12-15 hours while stirring. According to the patent data the benzoic acid yield reaches 15% of the weight of starting benzene.

Our investigation had two main fields of inquiry:

1) Interaction of benzene with carbon dioxide at super-high pressures in the absence of catalysts.

2) Effect of pressure on the reaction of benzene with carbon dioxide in presence of anhydrous aluminum chloride.

Investigation of the Reaction of Benzene with Carbon Dioxide at Super-High Pressures in Absence of Catalysts

Theoretical data were presented above to illustrate the extremely low equilibrium concentrations of benzoic acid when prepared from benzene and CO_2 even at very high pressures. We undertook a series of experiments in a super-high pressure apparatus with the aim of establishing whether this reaction proceeds in the absence of a catalyst.

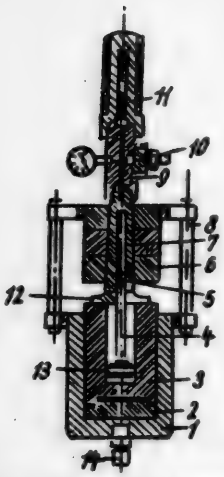

Fig. 1. Super-high pressure apparatus. 1) low-pressure cylinder; 2) packing of cylinder piston; 3) cylinder piston; 4) high-pressure piston; 5) packing of high-pressure cylinder; 6) reinforcing rings; 7) high-pressure cylinder; 8) column; 9) fitting to 12,000 atm pressure gage; 10) valve for feeding liquid into pressure apparatus; 11) reactor; 12) flange for connecting high-pressure cylinder to low-pressure cylinder; 13) packing of piston 4; 14) union for transmission of pressure to cylinder 1.

a) Experiments in steel ampoules with a moving piston. At first experiments were performed in a pressure apparatus* with a 15 cm^3 reactor capacity (Figure 1) into which was introduced an ampoule containing benzene and CO_2 and equipped with a moving piston (Figure 2). The ampoule was first placed in a Dewar flask containing a mixture of solid carbon dioxide and ether and then charged with solid carbon dioxide (1-2 g) and solid benzene (2-3 g). The ampoule was then closed with the piston and hollow nut and placed in the reactor of the pressure apparatus, after which pressure was developed in the reactor by means of a solution of water in glycerol. Experiments were performed at pressures of 7-8 thousand atm and temperatures of 125-200° over a period of 5 hours. Under these conditions no reaction of benzene with CO_2 was observed.

b) Experiments in a moving-piston reactor (without ampoule). The reactor was fitted with a moving piston and a valve for feeding gas; experiments were then performed in it at pressure up to 8-9 thousand atm and temperatures of 150-175° for 5 hours. The charge of benzene was here increased to 4.8-5.3 g. No products of interaction of benzene with CO_2 were detected.

Fig. 2. Ampoule with moving piston. 1) moving piston 2) stop nut.

c) Experiments in a large reactor. Experiments carried out in the pressure apparatus with a large reactor (approx. 50 cm^3) at 5-6 thousand atm and 125-150° for 5 hours likewise did not yield positive results. Finally, it was deemed necessary to try the effect of stirring of the mixture at super-high pressures.

d) Experiments in a rocking reactor. (Figure 3) were conducted at pressures up to 4500 atm and temperatures of 200 and 300°. At first the reactor was filled with dry carbon dioxide (dried in a high-pressure bomb over calcium chloride). Pressure was then created in the reactor by pumping in a mixture of dry, cryoscopically pure benzene and absolute ethanol or methanol; the pressure was then increased with the help of an intermediate vessel connected to a hydraulic compressor (Figure 4). Utilization of alcohols was necessitated by the solidification of pure benzene at pressures of about 900 atm at room temperature. It was established in preliminary experiments that benzene does not react with ethyl or methyl alcohol in the absence of a catalyst at pressures up to 6000 atm and temperatures of 200-300°.

The rocking reactor experiments likewise failed to yield positive results.

Consequently we were unable to establish the formation of benzoic acid or benzophenone from benzene and carbon dioxide at super-high pressures in absence of catalysts.

Investigation of Reaction of Benzene with Carbon Dioxide Under Pressure In Presence of Anhydrous Aluminum Chloride

We performed experiments in the rocking reactor (Fig. 3) constructed of stainless steel, capacity 130 cm^3, at pressures up to 2000 atm and at 100°. The reactor was charged with aluminum chloride and benzene, after which carbon dioxide (dried over calcium chloride in a high-pressure bomb for several days) was added. This

* The pressure apparatus was constructed in collaboration with L. F. Vereshchagin with assistance from Engineering Draughtsman A. A. Opekunov.

resulted in a pressure in the reactor of 80-100 atm ($P_{initial\ CO_2}$). Then with the help of a pump or intermediate vessel (Fig.4) a definite amount of benzene was pumped into the reactor until the required initial pressure ($P_{initial}$) was attained, following which the electric heater of the reactor was switched on. The duration of the experiment (τ) was reckoned to be from the moment of attainment of the required temperature (100°) to the switching-off of the heat.

After the reactor had cooled, the product was poured on to ice, extracted with ether, washed with water, and treated with 10% KOH solution; the alkaline solution was then separated and acidified with dilute hydrochloric acid. The separated residue of benzoic acid was filtered off and dried. The benzoic acid obtained had m.p. 107-110°. After recrystallization and sublimation it melted at 119-120°.

The ether solution was again washed with water until neutral and dried over calcined sodium sulfate; the ether was then driven off, followed by the benzene (in a water bath to a residual pressure of 20-25 mm). The residue (liquid product) was weighed and fractionated in vacuum at 1-2 mm. The 115-140° fraction was predominantly benzophenone. A second distillation of this fraction gave the benzophenone in the form of crystals identified by the preparation of the phenylhydrazone with m.p. 131-133° (the literature gives 134°).

The higher boiling fractions were hydrocarbons — products of reaction of benzene with anhydrous $AlCl_3$ [7], including crystalline 1,4-diphenyl-1,3-cyclopentadiene.

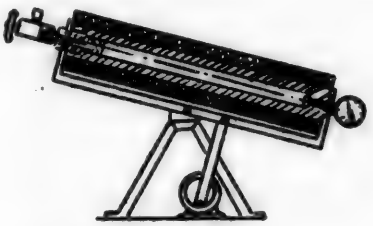

Fig. 3. Rocking reactor.

We may draw the following conclusions from the table:

1) Increase of pressure above 70-80 atm leads to an insignificant increase in the benzoic acid yield and to a more appreciable increase in the benzophenone yield.

2) An increase in the amount of anhydrous aluminum chloride causes a marked rise in the benzophenone yield.

DISCUSSION OF RESULTS

The above experimental data, together with the literature data, indicate that in the reaction of benzene with carbon dioxide in presence of anhydrous aluminum chloride, the latter enters into the reaction and thereby brings about the possibility of obtaining benzoic acid and benzophenone in yields many times greater than the equilibrium concentrations of these products as calculated from the change of free energy in the forward reactions: $C_6H_6 + CO_2 \rightleftarrows C_6H_5COOH$ and $2C_6H_6 + CO_2 \rightleftarrows (C_6H_5)_2CO + H_2O$.

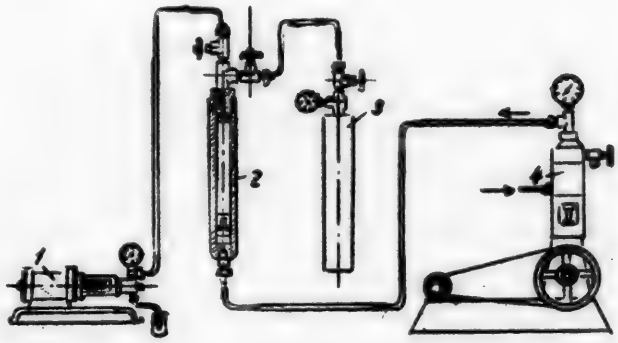

Fig. 4. Scheme for charging rocking reactor. 1) pump; 2) intermediate vessel; 3) rocking reactor; 4) hydraulic pump as designed by L. F. Vereshchagin

The effect of pressure on the course of the reaction between benzene and CO_2 in presence of $AlCl_3$ is, evidently, especially marked at low pressures when the density of the carbon dioxide sharply increases. Thus, according to the patent data [6] the passage of CO_2 for 30 hours through boiling benzene (600 g) in presence of 135 g $AlCl_3$ leads to the formation of 1.2 g C_6H_5COOH in all, while at 50 atm under the same conditions 40 g (i.e. 6.7%) benzoic acid and 4 g (0.7%) benzophenone are obtained. Our experiments showed that further increase of pressure has a very much weaker effect upon the benzoic acid yield; however, the benzophenone yield rises more appreciably

Interaction of Benzene with Dry Carbon Dioxide in Presence of $AlCl_3$ at 100° and τ = 5 hours

Expt. No.	C_6H_6 (g)	$AlCl_3$ (g)	Pressure			Yield (wt. % of benzene)			
			Initial CO_2 pressure in atm	Initial in atm	Mean in atm	C_6H_5COOH	Liquid products	Benzophenone fraction	Benzophenone
26a	40	20	40	40	78	6.0	16.3	3.5	3.0
38	73	40	95	320	620	5.9	24.2	8.8	7.8
37	75	40	100	375	900	6.5	23.1	11.7	8.4
39	73	40	90	490	1300	7.5			
42	77	40	90	850	2000	7.2	23.9	9.3	8.2
34	90	20	63	200	570	4.3	6.7	2.2	1.9
36	90	20	94	360	1270	3.7	6.6	2.5	2.1
43	75	50	80	600	1550	5.2	32.3	14.9	13.2

with the pressure than does the benzoic acid yield. We do not yet possess sufficient data to establish whether benzophenone formation proceeds through benzoic acid as intermediate product or whether it is an independent parallel reaction. It is more probable, however, that the formation of both benzoic acid and benzophenone occurs at the instant of decomposition of the respective complexes or chemical compounds formed with aluminum chloride. It is natural to assume that the formation of this type of complex (or compound), involving not one but two phenyl radicals, will be accompanied by a large contraction in volume, and this would also result in the much greater increase in the yield of benzophenone with rising pressure in comparison with the benzoic acid yield.

In conclusion the authors express their sincere thanks to Dr. L. F. Vereshchagin for his valuable advice in the completion of this investigation.

Mechanic V. A. Kuznetsov took part in the investigation.

SUMMARY

1. An investigation has been made of the system benzene-carbon dioxide at super-high pressures (up to 9000 atm) and elevated temperatures. No products of chemical interaction of the starting components could be detected.

2. The effect of pressures up to 2000 atm on the reaction of benzene with carbon dioxide in presence of anhydrous aluminum chloride was examined. Application of pressures exceeding 70-80 atm was found to lead to an insignificant increase in the benzoic acid yield. The benzophenone yield increases markedly with rising pressure. Increasing $AlCl_3$ content is accompanied by a considerable increase in the yield of benzophenone.

It was confirmed that aluminum chloride enters into chemical interaction with the starting components, and this fact indicates the possibility of performing reactions which in the absence of $AlCl_3$ proceed only with negligible yields under the investigated conditions of temperature and pressure.

LITERATURE CITED

[1] C. R. Kinney, Langlois, J. Am. Chem. Soc. 53, 2189 (1931).
[2] W. D. Bonner, C. R. Kinney, J. Am. Chem. Soc. 57, 2402 (1935).
[3] A. Michels, C. Michels, H. Wouters, Proc. Roy. Soc. 153, 214 (1935).
[4] A. Michels, A. Bijl, C. Michels, Proc. Roy. Soc. 160, 376 (1937).
[5] C. Friedel, I. M. Crafts, Comptes. rend. 86, 1368 (1878).
[6] German Pat. 524, 186 (1927); British Pat. 307, 223 (1928).
[7] M. G. Gonikberg and A. E. Gavrilova, J. Gen. Chem. 22, 1384 (1952); see Consultants Bureau translation, p. 1429.

Received January 23, 1951

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PROPERTIES OF 2-METHYL-4-PHENYL-2-PENTEN-4-OL OXIDE

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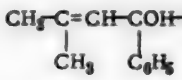
For the preparation of 2-methyl-4-phenyl-2,3-pentadiene we selected the Grignard reaction between mesityl oxide and phenyl magnesium bromide. This reaction has already been studied twice.

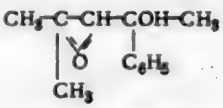
Klages [1] showed that mesityl oxide reacts normally with C_6H_5MgBr; however, in place of the unsaturated tertiary alcohol he obtained the product of its dehydration, 2-methyl-4-phenyl-2,3-pentadiene. Esafov [2] performed this reaction under very drastic conditions when the unstable reaction products undoubtedly suffered modification, and he obtained neither alcohol nor hydrocarbon; he also drew an incorrect conclusion about the course of the reaction.

Under our conditions the reaction proceeded normally and we obtained the unsaturated alcohol, 2-methyl-4-phenyl-2-penten-4-ol:



(I)

in yields of up to 70% of the calculated amount. We oxidized this alcohol with acetyl hydroperoxide with the aim of studying the properties of the alcohol-oxide:



(II)

since very few examples of such compounds are known and their properties have been inadequately studied.

α-Oxides are known to be characterized by addition reactions and by isomerization due to the cleavage of the oxide ring. The velocity of these processes, however, varies for α-oxides of different structures. For example, more energetic hydration takes place in the case of α-oxides whose oxide ring includes a tertiary carbon atom [3], while isomerizations to the corresponding aldehydes or ketones are more rapidly performed with α-oxides to whose oxide ring a phenyl radical is attached [4].

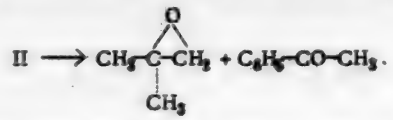
In his classic investigations of α-oxides, N. A. Prilezhaev [5] points out that the oxide ring of alcohol-oxides is stabilized by the hydroxyl group if the latter is in the α,β-position to the oxide ring. Hydration of the geraniol and linalool dioxides prepared by him only proceeded at the oxide ring remote from the hydroxyl group, and glyceryl oxides were then formed.

It must be pointed out that N. A. Prilezhaev also drew attention to a completely anomalous example – the oxide of allyl alcohol [6] which is readily hydrated to a glycerol. He explains this by the general rule of the difference between the first member of a series and its homologs.

In the present communication we describe an α-oxide which contains sharply contrasting functional groups. The oxide ring contains a tertiary carbon atom, susceptible to hydration; in the α,β-position to the oxide ring is the hydroxyl group which inhibits hydration; finally, the molecule of the alcohol-oxide contains a phenyl radical susceptible to the isomeric transformations of α-oxides. Such a diversity of functional groups in the alcohol-oxide prepared by us was clearly reflected in the properties of the α-oxide.

2-Methyl-4-phenyl-2-penten-4-ol was oxidized with 69.8% acetyl hydroperoxide in absolute ether. From the oxidation products was separated a crystalline substance with m.p. 55-56° whose analysis confirmed the presence of the alcohol-oxide (II). This compound proved to be extraordinarily unstable even at the ordinary temperature. A portion of the crystals of the alcohol-oxide was placed in a box in a desiccator over sulfuric acid for drying. After 7 days the whole of the material had been transformed into an oily liquid with the odor of acetophenone, which substance was also identified through the semicarbazone. No other decomposition product could be identified.

Over P_2O_5 and $CaCl_2$ the alcohol-oxide likewise broke down to acetophenone and a volatile substance with a rather sharp odor. This substance was apparently isobutene oxide, for the breakdown of our alcohol-oxide may be represented, by analogy with the known cleavage of some pinacones [7], by the following scheme:

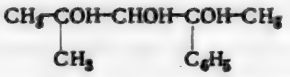


With the aim of identifying the second product of cleavage of the alcohol-oxide, we heated it in a Wurtz flask. Decomposition commenced at 200° with separation of a readily volatile substance with an unpleasant odor of rancid fats. The first distillates from the decomposition products gave a silver mirror, a semicarbazone with m.p. 124-125° and a crystalline product of condensation with dimedon melting at 151-152°. The analytical data for these crystals corresponded to the product of condensation of dimedon with isobutyraldehyde. The second product was acetophenone. This confirmed the foregoing scheme, for the isobutyraldehyde in the present case was undoubtedly the product of isomerization of 2-methylpropene oxide when heated.

The alcohol-oxide also fairly rapidly decomposed at room temperature when placed in dilute sulfuric acid. This was evident from the odor of the isobutyraldehyde formed. A second product, again, was acetophenone. Formation of isobutyraldehyde in sulfuric acid solution likewise undoubtedly proceeded via 2-methylpropene oxide and a series of intermediate reactions with sulfuric acid, in analogy with the behavior of ethylene oxide [8].

The alcohol-oxide also decomposed in semicarbazide solution, always forming acetophenone semicarbazone but no isobutyraldehyde semicarbazone. The absence of the latter is in accord with the findings of K. A. Krasusky [9] who reported that 2-methylpropene oxide does not isomerize to isobutyraldehyde in alkaline and neutral media.

Oxidation of 2-methyl-4-phenyl-2-penten-4-ol with acetyl hydroperoxide gave, in addition to the crystalline alcohol-oxide, a considerable amount of liquid product, probably the acetate of the trihydric alcohol,



We did not succeed, however, in isolating the pure substance since on vacuum distillation (4 mm) it broke down to acetophenone.

EXPERIMENTAL

Preparation of 2-methyl-4-phenyl-2-penten-4-ol (I). Into the 24 g magnesium in ether was slowly poured 152 g bromobenzene. At the conclusion of the reaction the mixture was heated for 30 minutes, and then, with ice-water cooling, 100 g mesityl oxide was poured in. The reaction mixture was again heated on the water bath for 30 minutes and left until the next day. By that time the flask contained a considerable amount of crystals and the ethereal solution had a yellow-orange color. The contents of the flask were cooled with ice-water and decomposed, first with a large amount of ice and then with dilute (1:3) sulfuric acid. The ether layer was separated and the aqueous layer subjected to two ether extractions. After drying over potassium carbonate, the ether was driven off and the substance (222 g) distilled at 20 mm to give the following fractions: I) 63-107° (24 g); II) 107-124° (17 g); III) 124-130° (133 g); IV) 130-140° (19 g); V) residue in flask (19 g).

In view of the fact that distillation at 130-140° (20 mm) was accompanied by appreciable decomposition of the substance with evolution of water, a second distillation of the third fraction was effected at 2 mm, at which pressure the substance came over at 91-92°.

n_D^{20} 1.5292; d_4^{20} 0.9777; MR_D 55.53; calculated 55.07.

0.1901 g substance: 0.5699 g CO_2; 0.1503 g H_2O. 0.1987 g substance: 24.39 ml CH_4 (0°, 760 mm). 0.1399, 0.2790 g substance; 19.53 g benzene: Δt 0.220°, 0.442°. Found %: C 81.76; H 8.84; OH 9.37; M 167.3, 166.1. $C_{12}H_{16}O$. Calculated %: C 81.82; H 9.09; OH 9.66; M 176.

Oxidation of 2-methyl-4-phenyl-2-penten-4-ol with acetyl hydroperoxide. 60 g alcohol in 100 ml absolute ether was oxidized with 38 g of 69.86% acetyl hydroperoxide. Oxidation proceeded

energetically with heat development, for which reason the hydroperoxide was added in small portions as the reaction progressed, and the reaction mixture was cooled with cold water. The temperature was held at 20-25°. At the end of one hour after completion of the addition, the reaction mixture contained 2.7 g unreacted hydroperoxide, and this amount was still unchanged on the following day. The whole mixture was therefore neutralized with 10% sodium carbonate, and then with dry sodium carbonate. The ether solution was dried over Na_2SO_4 and filtered; the ether was partly driven off and the residue retained for crystallization, a preliminary experiment having indicated the presence of a crystalline substance. After 4 days, 18.0 g white acicular crystals with the odor of camphor was obtained. The substance was very easily soluble in benzene, chloroform, carbon tetrachloride, methyl alcohol, ethyl alcohol, petroleum ether and other solvents. On recrystallization from ethyl alcohol it melted at 55-56°.

0.1879 g, 0.1963 g substance: 0.5177 g, 0.5388 g CO_2; 0.1438 g, 0.1488 g H_2O. 0.1727 g substance: 19.35 ml CH_4 (0°, 760 mm). 0.2095 g, 0.3781 g substance; 22.59 g benzene: Δt 0.236°, 0.468°. Found %: C 75.09. 74.86; H 8.56, 8.50; OH 8.54; M 181.2, 184.2. $C_{10}H_{18}O_2$. Calculated %: C 75.0; H 8.33; OH 8.85; M 192.

Distillation of the liquid products of oxidation (28.5 g) at 4 mm gave: I) 72-83° (10.4 g), n_D^{20} 1.5232; II) 83-105° (2.0 g), n_D^{20} 1.5239; III) 105-120° (5.3 g), n_D^{20} 1.5290; IV) resinous residue (10.8 g). The substance in the first three fractions was acetophenone. At the ordinary pressure it distilled at 198-200°; it gave a semicarbazone with m.p. 197-199° which did not depress the melting point of acetophenone semicarbazone.

Cleavage of the alcohol-oxide over sulfuric acid. 1.5 g of the alcohol-oxide was placed in a desiccator over sulfuric acid. After two days there was appreciable formation of a liquid product with the odor of acetophenone, and after 7 days no crystals of the oxide remained. The liquid product boiled at 3 mm pressure at 61-63° and at the ordinary pressure at 200-202°.

n_D^{20} 1.5220; d_4^{20} 1.0431; MR_D 35.5. $C_9H_{10}O$; calculated 35.08.

The substance gave a semicarbazone with m.p. 198-199° which did not depress the m.p. of authentic acetophenone semicarbazone. We were unable to isolate other products of the cleavage of the alcohol-oxide, although a readily volatile substance was undoubtedly present, as indicated by the frothing of the liquid at the start of distillation in vacuum.

Cleavage of the alcohol-oxide over $CaCl_2$ and P_2O_5. Two lots of 2.0 g of alcohol-oxide crystals were placed in separate desiccators over $CaCl_2$ and P_2O_5 respectively. After a week both lots of crystals had been converted into liquid, and after 10 days they had completely disappeared. The air in the desiccators (containing a substance with a fairly sharp odor) was sucked through solutions of semicarbazide and dimedon, but neither a semicarbazone nor a dimedon condensation product was obtained. The liquid which had formed, smelling of acetophenone, distilled at 199-201° and gave a semicarbazone melting at 199-200° which did not depress the melting point of authentic acetophenone semicarbazone.

Cleavage of the alcohol-oxide by heating. 2.0 g of crystals of alcohol-oxide was heated in a flask over a bare flame. The crystals melted and then cleavage of the alcohol-oxide took place at 200°; the unpleasant odor of rancid fat was clearly evident. The first fractions from distillation came over at 70-100° and were collected in semicarbazide solution, dimedon and ammoniacal silver oxide solution. With the last-named a magnificent silver mirror was quickly formed. The solution of semicarbazide containing the cleavage product was heated on the water bath for about an hour, giving on cooling a semicarbazone melting at 124-125°, which agreed with the literature data [10] for isobutyraldehyde. The dimedon solution containing the aldehyde was heated for 3 hours on the water bath. Snow-white acicular crystals came down within few hours after cooling, and these melted (after recrystallization from ethyl alcohol) at 151-152°. Since the literature does not mention the product of condensation of isobutyraldehyde with dimedon, we carried out its analysis:

0.1580 g substance: 0.4141 g CO_2; 0.1260 g H_2O. Found %: C 71.48; H 8.92. $C_{20}H_{32}O_4$. Calculated %: C 71.85; H 8.98.

A second product distilled over at 198-200° and when collected in semicarbazide solution it gave a semicarbazone melting at 199-200°. It did not depress the melting point of authentic acetophenone semicarbazone.

Cleavage of the alcohol-oxide in sulfuric acid solution. 10 ml of 0.1 N sulfuric acid was poured into 1.6 g of the alcohol-oxide. In 15-20 minutes the odor of isobutyraldehyde was noticed and the crystals had been replaced by liquid. On the following day there was no trace of crystals. At the bottom

of the test-tube was a layer of oily substance with the odor of acetophenone, and a strong smell of rancid fat came from the test-tube. With semicarbazide the substance of the bottom layer gave a semicarbazone with m.p. 197-199°; it did not depress the m.p. of acetophenone semicarbazone. The second cleavage product, with the odor of isobutyraldehyde, was distilled into an alcoholic solution of dimedon. Heating for two hours, followed by cooling resulted in separation of snow-white acicular crystals which melted at 150.5-151°. No melting point depression occurred after mixing these crystals with those obtained by condensing dimedon with the product of cleavage of the alcohol-oxide by heating.

SUMMARY

1. Synthesis was effected from phenyl magnesium bromide and mesityl oxide of the unsaturated alcohol 2-methyl-4-phenyl-2-penten-4-ol in 75% yield.

2. Oxidation of 2-methyl-4-phenyl-2-penten-4-ol with acetyl hydroperoxide gave its oxide.

3. It was established that the oxide of 2-methyl-4-phenyl-2-penten-4-ol is extremely unstable. In a desiccator over H_2SO_4, $CaCl_2$ and P_2O_5, also on heating and in sulfuric acid solution, it splits up into acetophenone and 2-methylpropene oxide.

LITERATURE CITED

[1] Klages, Chem.Zentr., II, 215 (1904); Ber., 37, 2301 (1904).

[2] Esafov, J. Gen. Chem. 9, 468 (1939).

[3] Eltekov, J. Russ. Chem. Soc. 14, 355 (1882).

[4] Levy and Lagrave, Comptes. rend. 180, 1032 (1925); Lagrave, Ann. Chim. et Phys., 8, 363 (1927); Tiffeneau, Comptes. rend. 140, 1459 (1905); 141, 663 (1906); Klages, 39, 1754 (1906); Pansevich and Timoshek, J. Gen. Chem. 22, 147 (1952);*

[5] N. A. Prilezhaev, J. Russ. Chem. Soc. 44, 613 (1912).

[6] N. A. Prilezhaev, J. Russ. Chem. Soc. 43, 609 (1911).

[7] E. D. Venus-Danilova and L. A. Pavlova, J. Gen. Chem. 19, 1754 (1949);** Zagumennyi, J. Russ. Chem. Soc. 4, 354(1872); 7, 46 (1875); Thorner and Zincke, Ber., 10, 1474, 1476 (1877); Meerwein, Ann. 396, 246 (1913).

[8] A. E. Favorsky, Collected Works, 182 (1940).

[9] K. A. Krasusky, J. Russ. Chem. Soc. 34, 301, 547 (1902).

[10] Beilstein, 1 (1), 349.

Received December 28, 1950

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*See Consultants Bureau translation, p. 179.

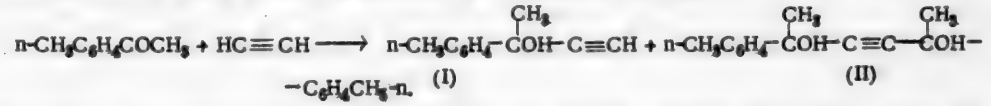
**See Consultants Bureau translation, p. a-197.

SYNTHESIS OF METHYL p-TOLYLETHINYL CARBINOL AND ITS DERIVATIVES

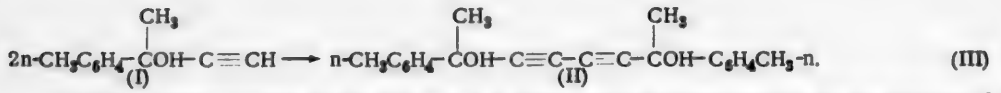
A. I. Lebedeva and T. A. Mishnina

Propargyl alcohol, first prepared in 1872 [1], is the simplest representative of the homologous series of monohydric acetylenic alcohols. Other representatives of the series have been synthesized by very different methods. Tertiary acetylenic alcohols can be prepared in good yield by A. E. Favorsky's method [2] of condensation of various ketones with acetylene in presence of powdered potassium hydroxide. Relatively little attention has so far been given, however, to the reaction of acetylene with alkaryl ketones. We know that acetophenone does not react with acetylene in presence of powdered potassium hydroxide [3]. It was possible, however, to obtain 2% of methylphenylethinyl carbinol from acetophenone and acetylene in presence of sodium amide [4]. This yield could be increased to 7% by reacting acetophenone with sodium acetylide in liquid ammonia [5].

We decided to investigate the condensation of methyl-p-tolyl ketone with acetylene in presence of potassium hydroxide powder and to examine the influence of the p-tolyl radical on the velocity of this reaction. Preliminary experiments showed that methyl-p-tolyl ketone is more reactive than acetophenone when the reaction with acetylene is performed under the usual conditions. The main reaction product was di-p-tolyl-2,5-hexyne-3-diol-2,5 (II) in the form of three isomers with different melting points, together with a small amount of methyl p-tolyl-ethinyl carbinol (I) in admixture with the original ketone [6]. In this investigation we succeeded in raising the yield of methyl p-tolylethinyl carbinol to 50% by adopting the procedure of I. A. Favorskaya and L. V. Fedorova [7] of greatly increasing the dilution of the ketone with the solvent and decreasing the rate of its addition to the reaction mass. In this manner more favorable conditions were created for the formation of the acetylenic alcohol. But notwithstanding the great dilution and the rapid flow of acetylene, the product of the reaction always consisted of a mixture of methyl- p-tolyl-ethinyl carbinol (I), methyl p-tolyl ketone and dimethyl di-p-tolylbutyne diol (II):



The mixture of products was subjected to distillation under reduced pressure when a liquid came over consisting of starting ketone and the acetylenic alcohol. The higher boiling fraction isolated by fractional distillation was treated with a solution of semicarbazide acetate (for removal of traces of the initial ketone) and then left in the cold for a long period when very large regular crystals came down. These melted, after purification, at 34-35°. The aqueous alcoholic solution of the crystals was decolorized with aqueous permanganate and gave a white precipitate with ammoniacal silver oxide solution. Results of carbon and hydrogen determinations, of molecular weight and molar refraction determinations (the latter in supercooled solution), and of the determination of the percent content of active hydrogen (Terentiev-Shcherbakova method) showed that we had actually obtained the acetylenic alcohol, methyl p-tolylethinyl carbinol. A weighed sample of the substance was hydrogenated in presence of platinum, when addition occurred of 102 % of hydrogen (on the theoretically calculated amount) Hydrogenation yielded a saturated alcohol, methylethyl p-tolyl carbinol, boiling at 99-100° (5 mm). Its principal constants were determined. For comparison the synthesis was then effected of authentic methylethyl p-tolyl carbinol from p-bromotoluene and methylethyl ketone. From methyl p-tolylethinyl carbinol (I) was obtained, by the method of Zalkind and Aizikovich [8] the corresponding diacetylenic glycol, di-p-tolyl-2,7-octadiyne-3,5-diol-2,7 (III). Formation of the glycol was only observed, however, after passage of an oxygen stream and after a few hours had elapsed following the addition of the methyl p-tolylethinyl carbinol. On driving off the ether, a crystalline mass remained which could be separated into two isomers: the first in the form of lustrous platelets which turned dull on standing and melted at 129-130°; the second in the form of needlets melting at 136-137°. The aqueous alcoholic solutions of both isomers were decolorized with aqueous permanganate. Each of the isomers was analyzed for content of carbon, hydrogen and active carbon. The results conformed to di-p-tolyl-2,7-octadiyne-3,5-diol-2,7 (III), which was obtained in about 82% yield:



Catalytic hydrogenation of the first isomer in presence of platinum resulted in the addition of 100.6% hydrogen with formation of a saturated glycol in the form of snow-white flakes with a pearly irridescence, melting at 77-78°. The analysis corresponded to di-p-tolyl-2,7-octanediol,2-7. Catalytic hydrogenation of the second isomer of di-p-tolyl-2,7-octadiyne-3,5-diol-2,7 in presence of platinum resulted in addition of 100.3% hydrogen with formation of a white, finely crystalline powder with m.p. 114.5-115.5°. Analysis of this saturated glycol showed it to correspond to another isomer of di-p-tolyl-2,7-octanediol-2,7.

It is known from the literature that the melting points of tertiary acetylenic alcohols and the corresponding starting ketones are nearly always close to one another. This is clearly illustrated by the table following. On the basis of these data it was possible to predict that the acetylenic alcohol obtained from methyl p-tolyl ketone (m.p. 28°) would have a low m.p. close to room temperature, and to infer that the m.p. of 120-121° given by Iremadze[12] for methyl p-tolylethinyl carbinol was extremely dubious. From our own results it is seen that Iremadze did not obtain methyl p-tolylethinyl carbinol when he reacted methyl p-tolyl ketone with acetylene, but a mixture of the isomers of di-p-tolyl-2,5-hexyne-3-diol-2,5 with which all the subsequent investigation was performed.

Starting ketones	M.p.	Literature	Acetylenic alcohols	M.p.	Literature
Acetophenone	20.5°	[9]	Methylphenylethinyl carbinol	49°	[10]
Benzophenone	49	[9]	Diphenylethinyl carbinol	44.5	[10]
Methyl p-tolyl ketone	28	[9]	Methyl p-tolylethinyl carbinol	34-35	[4,11]
Di-p-tolyl ketone	90-95	[7]	Di-p-tolylethinyl carbinol	86-87	[7]

EXPERIMENTAL

Preparation of methyl p-tolyldiethinyl carbinol. Into a three-necked flask fitted with a powerful propeller-type stirrer were introduced 250 g potassium hydroxide powder and 300 ml absolute ether. While a continuous stream of acetylene was passed in under external cooling with ice-water, addition was made to the reaction mass of 40 g methyl p-tolyl ketone in 600 ml absolute ether. The methyl p-tolyl ketone was prepared from methyl p-tolyl carbinol through p-toluidine and p-bromotoluene. The boiling point of the ketone (9 mm) was 94-95°. The ketone was added over a period of 10 hours. The reaction mass was left overnight and then decomposed with iced water. The separated ether layer was saturated with carbon dioxide and dried with sodium sulfate; the ether was then evaporated.

The residue was distilled in vacuum. Fraction I (12.0 g) boiled at 92° (7 mm), and at 96° (3 mm); fraction II (34.7 g) at 97° (3 mm); the residue in the flask (4.2 g) crystallized.

The aqueous alcoholic solution of the second fraction gave a precipitate with ammoniacal silver oxide solution and with aqueous permanganate solution. The liquid gave a precipitate with an acetic acid solution of semicarbazide. In order to remove traces of the original methyl p-tolyl ketone, the whole of the liquid product was treated with an acetic acid solution of semicarbazide, and the semicarbazone precipitate was filtered and recrystallized from alcohol. Its m.p. of 202-203° corresponded to that of methyl p-tolyl ketone semicarbazone. The filtrate was extracted with ether, and the ether extract washed with soda solution and dried with sodium sulfate. Removal of the ether left 22.7 g methyl p-tolylethinyl carbinol boiling at 103.5° (5 mm) and crystallizing on standing in the cold. The crystals melted at 34-35° (from petroleum ether with b.p. 40-80°). The crystals were 1-2 cm in length. The yield of acetylenic alcohol (allowing for the unreacted ketone) was 69.0% of theory.

$d_4^{20.8}$ 1.0066; d_4^{20} 1.0088; $n_\alpha^{20.8}$ 1.52832; $n_\beta^{20.8}$ 1.54271; n_D^{20} 1.5310; MR_α 49.03; MR_β 50.14; MR_D 49.13. $C_{11}H_{12}OF_3F$. Calculated MR_α 48.55; MR_β 49.71; MR_D 48.92.

0.1152 g substance: 0.3488 g CO_2; 0.0794 g H_2O. 0.1110 g substance: 0.3360 g CO_2; 0.0770 g H_2O. 0.0945 g substance; 18.00 g benzene: Δt 0.174°. 0.2288 g substance: 18.00 g benzene: Δt 0.422°. 0.1346 g substance: 20.7 ml CH_4 (20°, 763.1 mm). 0.1273 g substance: 18.4 ml CH_4 (20°, 763.1 mm). Found %: C 82.57, 82.55; H 7.71, 7.76; M 156.3, 156.0; active H-atoms 1.006, 1.008. $C_{11}H_{11}OH$. Calculated %: C 82.46;

H 7.51; M 160.2; active H-atoms 1.000.

Catalytic hydrogenation of methyl p-tolylethinyl carbinol. 5.00 g substance: 0.5 g Pt, 60 ml alcohol. Hydrogenation was performed for 1 hour 20 minutes.

Addition took place of 1425 ml H_2 (0°, 760 mm) equivalent to 101.9%. $C_{11}H_{12}O$. Calculated 1398.2 ml H_2.

After distilling off the alcohol there remained 4.1 g liquid boiling at 99-100° (5 mm) which did not form a precipitate with ammoniacal silver oxide solution and did not decolorize permanganate.

n_D^{20} 1.5158; d_4^{20} 0.9691; MR_D 51.16. $C_{11}H_{16}OF_3$. MR_D 50.92.

0.0941 g substance: 0.2783 g CO_2; 0.0814 g H_2O. 0.1069 g substance: 0.3157 g CO_2; 0.0932 g H_2O. 0.1800 g substance: 27.8 ml CH_4 (23.5°, 765 mm). 0.1318 g substance: 20.6 ml CH_4 (23.5°, 765 mm). Found %: C 80.65, 80.54; H 9.68, 9.76; active H-atoms 1.019, 1.032. $C_{11}H_{15}OH$. Calculated %: C 80.45; H 9.82; active H-atoms 1.000.

Preparation of methylethyl p-tolyl carbinol. Methylethyl p-tolyl carbinol was prepared for comparison purposes from methylethyl ketone and p-bromotoluene. To 7.6 g Mg was added 53.5 g p-bromotoluene in 150 ml ether, and then 22.3 g methylethyl ketone in 50 ml ether. Removal of the ether left a residue of liquid boiling at 93-93.5° (3 mm).

n_D^{20} 1.5174; d_4^{20} 0.9726; MR_D 51.11. $C_{11}H_{16}OF_3$. Calculated MR_D 50.92.

0.1629 g substance: 0.4792 g CO_2; 0.1416 g H_2O. 0.1092 g substance: 0.3219 g CO_2; 0.0960 g H_2O. 0.1639 g substance: 25.7 ml CH_4 (17°, 760.6 mm), 0.1240 g substance: 20.0 ml CH_4 (17.5°, 760.6 mm). Found %: C 80.23, 80.15; H 9.72, 9.84; H-atoms 1.075, 1.102. $C_{11}H_{15}OH$. Calculated %: C 80.45; H 9.82; active H-atoms 1.000.

Analysis of di-p-tolyl-2,5-hexyne-3-diol-2,5. The solid residue after distillation of the methyl p-tolyl ketone and the methyl p-tolylethinyl carbinol amounted to 4.2 g and was recrystallized from benzene; it then melted at 121-123° and did not depress the melting point of a previously prepared and characterized mixture of the isomers of di-p-tolyl-2,5-hexyne-3-diol-2,5 [6].

0.1077 g substance: 18.3 ml CH_4 (18°, 749.6 mm). 0.1045 g substance: 18.1 ml CH_4 (18°, 749.6 mm). Found: active H-atoms 2.024, 2.067. $C_{20}H_{22}(OH)_2$. Calculated: active H-atoms 2.000.

Preparation of di-p-tolyl-2,7-octadiyne-3,5-diol-2,7. 40 g Cu_2Cl_2 was mixed with 100 g NH_4Cl and to the mixture was added 400 ml water, 1.5 ml HCl and 10 g methyl p-tolylethinyl carbinol in 100 ml alcohol. The mixture was stirred in the course of 10 hours with continuous passage of a stream of oxygen (with a stream of air the diacetylenic glycol was formed only after several days). At the end of the day a white, clotted solid had formed at the surface of the mixture and was extracted with ether. The extract was dried over calcined potassium carbonate. The residue (after driving off the ether) was a syrupy liquid which crystallized on standing. After drying in the vacuum desiccator, the crystals melted at 106-111°. The amount was 8.1 g (81.5% of the theoretical yield). Repeated recrystallizations from benzene and from a mixture of benzene and petroleum ether (b.p. 40-75°) yielded two fractions of crystals: I) m.p. 129-130°, in the form of small scales; II) m.p. 136-137°, in the form of needlets.

Neither fraction gave a precipitate with ammoniacal silver oxide solution or decolorized an aqueous alcoholic solution of permanganate.

Analysis of the diacetylenic glycol with m.p. 129-130° (from benzene):

0.1075 g substance: 0.3282 g CO_2; 0.0679 g H_2O. 0.1105 g substance: 0.3372 g CO_2; 0.0702 g H_2O. 0.2857 g substance: 15.00 g dioxane: Δt 0.275°. 0.4104 g substance: 15.00 g dioxane: Δt 0.410°. 0.0819 g substance: 12.4 ml CH_4 (20°, 763.1 mm). 0.0796 g substance: 12.2 ml CH_4 (20°, 763.1 mm). Found %: C 83.26, 83.22; H 7.07, 7.11; M 325.5, 313.6; active H-atoms 1.995, 2.019. $C_{22}H_{22}(OH)_2$. Calculated %: C 83.05; H 6.96; M 318.4; active H-atoms 2.000.

Catalytic hydrogenation of ditolyloctadiynediol with m.p. 129-130°. 3.00 g substance: 1.4 g Pt, 70 ml alcohol. Duration of hydrogenation 2 hours 35 minutes. Addition occurred of 850.9 ml H_2 (0°, 760 mm), 100.6%. $C_{22}H_{22}O_2$. Calculated 846 ml H_2.

Removal of the alcohol left 2.9 g of a transparent viscous mass which crystallized in the course of three days. After two recrystallizations from petroleum ether (boiling range 40-75°) with a few drops of benzene, separation took place of crystals in the form of nacreous starlets with m.p. 77-78°. The obtained glycol did not decolorize an alcoholic solution of permanganate. A mixed sample with the original glycol melted at 107-122°.

0.1278 g substance: 0.3809 g CO_2; 0.1068 g H_2O. 0.1256 g substance: 0.3740 g CO_2; 0.1059 g H_2O. 0.1017 g substance: 14.8 ml CH_4 (21°, 762.1 mm). 0.1109 g substance: 15.6 ml CH_4 (21°, 760.1 mm). Found %: C 81.28, 81.21; H 9.35, 9.43; active H-atoms 1.862, 1.856, $C_{22}H_{26}(OH)_2$. Calculated %: C 80.94; H 9.26; active H-atoms 2.000.

Analysis of the diacetylenic glycol with m.p. 136-137° (from benzene-petroleum ether mixture).

0.1010 g substance: 0.3066 g CO_2; 0.0630 g H_2O. 0.1079 g substance: 0.3280 g CO_2; 0.0681 g H_2O. 0.0735 g substance: 11.0 ml CH_4 (20°, 763.1 mm). Found %: C 82.79, 82.90; H 6.98, 7.06. Found: number of active H atoms 2.000.

Catalytic hydrogenation of ditolyloctadiynediol with m.p. 136-137°. 0.70 g substance: 0.3 g Pt; 35 ml alcohol. Hydrogenation period 1 hr.5 min. Addition of 202.6 ml H_2 (0°, 760 mm), 100.3%, $C_{22}H_{22}O_2$. Calculated 197.0 ml H_2.

Removal of the alcohol left 0.7 g crude crystals. Recrystallization from a mixture of benzene and petroleum ether gave a white, powdery crystalline mass with m.p. 114.5-115.5°. A mixture with the original diacetylenic glycol melted at 100-105°; a mixture with the saturated glycol obtained from the first fraction melted at 70-100°.

0.1031 g substance: 0.3065 g CO_2; 0.0855 g H_2O. 0.0984 g substance: 15.6 ml CH_4 (23.5°, 765.3 mm). Found %: C 81.08; H 9.28; number of active H atoms 2.081. $C_{22}H_{26}(OH)_2$. Calculated %: C 80.94; H 9.26; number of active H atoms 2.000.

SUMMARY

1. Methyl p-tolyl ketone reacts with acetylene under Favorsky's reaction condition to give the tertiary acetylenic alcohol, methyl p-tolylethinyl carbinol, and the acetylenic glycol, symm. dimethyl di-p-tolylbutynediol.

The yields of alcohol and glycol vary with the reaction conditions, in particular the dilution and rate of addition of the methyl p-tolyl ketone.

2. Catalytic hydrogenation of methyl p-tolylethinyl carbinol in presence of platinum gave the saturated alcohol, methylethyl p-tolyl carbinol, which was characterized.

3. Methyl p-tolylethinyl carbinol can be converted by the method of Yu. S. Zalkind and M. A. Aizikovich into the diacetylenic glycol, di-p-tolyl-2,7- octadiyne-3,5-diol-2,5. Two forms of this glycol were isolated.

4. Catalytic hydrogenation of di-p-tolyl-2,7-octadiyne-3,5-diol-2,7 in presence of platinum gave two forms of the saturated glycol, di-p-tolyl-2,7-octadiol-2,7, which were characterized.

LITERATURE CITED

[1] L. Hewry, Ber., 5, 453, 569 (1872); 14, 404 (1881).

[2] A. E. Favorsky, Author's Certificate No. 31017.

[3] A. I. Lebedeva and V. A. Shlyakova, J. Gen. Chem. 19, 1290 (1949); see Consultants Bureau trans., p.1285.

[4] W. H. Carothers and D. D. Coffman, J. Am. Chem. Soc. 54, 4071 (1932).

[5] K. N. Campbell, B. K. Campbell and L. T. Eby, J. Am. Chem. Soc. 60,2882 (1938).

[6] A. I. Lebedeva and R. P. Ryskina, J. Gen. Chem. 20, 1868 (1950); see Consultants Bureau trans., p. 1933.

[7] I. A. Favorskaya and L. V. Fedorova, J. Gen. Chem. 20, 1068 (1950); see C.B.translation, p. 1109.

[8] Yu. S. Zalkind and M. A. Aizikovich, J. Gen. Chem. 7, 227 (1937).

[9] Dictionary of Organic Chemistry, Vol. I, II [1949].

[10] Ch. H. Hurd and R. E. Christ, J. Am. Chem. Soc. 59, 118 (1937); Yu. S. Zalkind and A. P. Ivanov, J. Gen. Chem. 11, 803 (1941).

[11] V. P. Teterin and A. P. Ivanov, J. Gen. Chem. 7, 1629 (1937).

[12] Yu. S. Zalkind and N. Iremadze, J. Gen. Chem. 18, 1554 (1948).

Received December 30, 1950

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ADDITION OF HYDROGEN TO ACETYLENE DERIVATIVES

INVESTIGATION OF THE VELOCITY OF HYDROGENATION OF 1,4-BUTYNEDIOL AND ITS ACETATE

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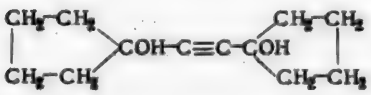
The catalytic hydrogenation of γ-acetylenic glycols, both ditertiary and disecondary, has been studied with reference to many substances by Yu. S. Zalkind and his pupils [1]. They showed that the velocity of hydrogenation of γ-acetylenic glycols in presence of colloidal palladium sharply slows down after addition of two atoms of hydrogen. This effect becomes increasingly marked with increasing radical length and molecular volume. In presence of platinum the velocity of hydrogenation falls off steadily without any discontinuity in the curve. Yu. S. Zalkind explained [2] the abrupt slowing-down of the reaction in the first case by closure of the ring by the hydrogen bond. After formation of the double bond, a ring is formed at the expense of the hydrogen of the hydroxyl groups which hinders access of the hydrogen atoms to the double bond.

The objective of the present investigation was the study of the velocity of hydrogenation of a substance in which no effect would be exercised by radicals, i.e. one in which steric hindrance would be excluded during the reaction. For this purpose we chose 1,4-butynediol and its acetate. This glycol has already [3] been hydrogenated both with platinum and palladium, but the authors were not interested in the velocity of hydrogen addition. According to the literature data, the hydrogenation of 1,4-butynediol proceeds more energetically when using palladium as catalyst (and ether as solvent) than when using platinum, and in the further course of hydrogenation the hydroxyl groups of the glycol are substituted by hydrogen with formation of a hydrocarbon. We have confirmed this process.

The experiments here performed have shown that the behavior of 1,4-butynediol is quite different from that of disecondary and ditertiary γ-acetylenic glycols. Firstly, it is hydrogenated very slowly (Table 1); secondly, in presence of colloidal palladium, after addition of two hydrogen atoms there is no discontinuity in the rate of addition.

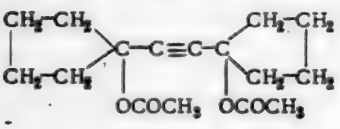
TABLE 1

Formula of the γ-glycols	Amount of palladium catalyst (in mg)	Amount of solvent (in ml)	Reaction temp.	Amount of glycol (in mole)	Period of addition of hydrogen (in minutes)
$CH_2OH-C\equiv C-CH_2OH$	10	50	20°	0.01	45
$CH_3-CHOH-C\equiv C-CHOH-CH_3$	5	50	24	0.01	6
$C_6H_5-CHOH-C\equiv C-CHOH-C_6H_5$	5	50	16	0.01	5
$(CH_3)_2COH-C\equiv C-COH(CH_3)_2$	5	50	18	0.01	10
$(C_2H_5)_2COH-C\equiv C-COH(C_2H_5)_2$	5	50	19	0.01	145 (78.4%)
	5	50	20	0.001	7

Regarding 1,4-butynediol acetate, the velocity of hydrogenation is here greater than for butynediol (Table 2); here also a discontinuity does not arise after addition of one molecule of hydrogen.

The results demonstrate that in the diprimary glycols, ring-closure by the hydrogen bond is excluded and the triple bond is more stable (due to the influence of the charged protons).

TABLE 2

Acetates of γ-acetylenic glycols	Amount of palladium catalyst (in mg)	Amount of solvent (in ml)	Reaction temp.	Amount of ester (in mole)	Period of addition of hydrogen (in min.)
$CH_3COOCH_2-C\equiv C-CH_2OOCCH_3$	5	50	26°	0.01	18
$CH_3-CH(OCOCH_3)-C\equiv C-CH(OCOCH_3)-CH_3$	10	50	14	0.01	5.5
$CH_3-C_6H_4-CH(OCOCH_3)-C\equiv C-CH(OCOCH_3)-C_6H_4-CH_3$	5	50	16	0.01	4 min.46 sec.
	5	50	18	0,01	9

Comparison of the rate of addition of hydrogen to 1,4-butynediol acetate with the rate of addition to other acetates of γ-acetylenic glycols shows that 1,4-butynediol acetate adds on hydrogen much more slowly (Table 2).

EXPERIMENTAL

Synthesis of butynediol acetate. A mixture of 10 g butynediol (m.p. 58°), 30 ml acetic anhydride and 1 g calcined sodium acetate was heated with constant stirring on the water bath at 98° for 13 hours. On pouring the reaction mass into water, an oily, brown-colored liquid was obtained which was washed with sodium bicarbonate solution and with water and then extracted with ether. After the ether had been evaporated, the substance distilled at 130-130.5° (14 mm) and consisted of a glycerol-like, colorless liquid. This crystallized on standing and formed transparent platelets with m.p. 31-32°. Yield 12 g or 42.4% of theory.

d_{20}^{20} 1.1265; n_D^{20} 1.4547; MR_D 40.92; calculated 40.45.

12.02 mg substance: 24.79 mg CO_2; 6.74 mg H_2O. 14.41 mg substance: 28.85 mg CO_2; 7.71 mg H_2O. 0.0904 g substance; 17.19 g benzene: Δt 0.155°. 0.019 g substance; 0.2344 g camphor: Δt 19.5°. Found %: C 56.29, 56.48; H 6.27, 6.18; M 164, 173.2. $C_8H_{10}O_4$. Calculated %: C 56.47; H 5.88; M 170.

Catalytic hydrogenation of 1,4-butynediol. Butynediol (m.p. 58°) which had been recrystallized from ether was hydrogenated in presence of colloidal palladium on wheat starch. The activity of the palladium was tested on tetramethylbutynediol which in presence of 5 mg of the palladium added on 2 atoms of hydrogen in the course of 12 minutes. Hydrogenation was also carried out with platinum black; ethyl alcohol was used as solvent. In Table 3 are set out the results of three experiments on glycol hydrogenation with 5, 10 and 20 mg palladium. The experiments were performed at 22°, using 50 ml of solvent (ethyl alcohol); in all of the experiments H_2 = 256 ml (quantity of hydrogen in milliliters required for conversion of an acetylenic glycol into an olefinic glycol); t = duration of experiment (in minutes).

TABLE 3

Expt. No.	t / Pd(in mg)	3	6	9	12	15	18	21	24	27	30	33	36	51	102
1	5	20	32	43	52	61	70	79	88	97	106	115	134	–	271
2	10	41	61	79	96	113	130	147	161	175	188	201	–	–	279
3	20	40	68	94	118	142	166	189	211	233	255	275	–	–	–

As we see from Table 3, hydrogenation with palladium proceeds slowly and uniformly without any discontinuity. On interrupting the hydrogenation reaction in presence of palladium after combination of

two hydrogen atoms, an olefinic glycol is obtained in the form of a liquid boiling at 144-146° (21 mm); n_D^{20} 1.4700; d_{20}^{20} 1.0876; MR_D 23.26; calculated 23.25. The constants agree with the literature data.

Hydrogenation with platinum black (Table 4) also proceeds without a discontinuity; after addition of two hydrogen atoms (necessary to convert the triple bond into a double one) hydrogenation proceeded further at the expense of substitution of the hydroxyl groups.

TABLE 4 •

t . . .	3	6	9	12	15	18	21
v . . .	127	117	101	64	81	47	50
V. . .	127	244	345	409	537		
$2H_2$ (%)	25.1	48.2	68.2	80.8	96.8		

NOTE. t is the duration (in min. from start of experiment); v is the hydrogen vol. (in ml) absorbed during the preceding period; V is the volume absorbed from the start of the experiment.

Catalytic hydrogenation of 1,4-butynediol acetate in presence of colloidal palladium. Hydrogenation of the acetate (b.p. 130-131.5° at 14 mm) was effected under the same conditions as for 1,4-butynediol; the catalyst was from the same preparation. Table 5 gives the data for experiments with 5 and 10 mg of palladium. Temperature 26°; 50 ml ethyl alcohol for each experiment; H_2 = 262 ml (amount of hydrogen needed for conversion of the triple bond into the double one).

TABLE 5

Expt. No.	Pd (in mg) \ t	3	6	9	12	15	18	21	24	27	30	33	36
1	5	58	100	142	184	226	268	309	350	391	419	441	542
2	10	60	134	202	202	327	–	–	–	542	–	–	–

It is clear from Table 5 that hydrogenation proceeds uniformly without a discontinuity, and after addition of two molecules of hydrogen the reaction proceeds further, in all probability at the expense of reduction of the ester.

1,4-Butynediol acetate was also hydrogenated in presence of platinum black.

TABLE 6 ••

t	3	6	9	12	15
v	110	180	159	139	64
V. . . .	110	290	449	588	652
$2H_2$ (%)	21	55.3	85.6		

Table 6 indicates that under the same conditions butynediol acetate is hydrogenated uniformly without any discontinuity and more rapidly than butynediol.

After addition of two atoms of hydrogen (in presence of palladium) the reaction was broken off. On working up the hydrogenation product, a colorless liquid (b.p. 128-129° at 25 mm) was obtained.

n_D^{20} 1.4430; d_{20}^{20} 1.0848; MR_D 42.04; calculated 41.98.

3.862 mg substance: 7.985 mg CO_2; 2.493 mg H_2O. 4.100 mg substance: 8.370 mg CO_2; 2.015 mg H_2O. 0.2268 g substance; 18.80 g benzene: Δt 0.345°. Found %: C 55.79, 55.71; H 7.22, 7.14; M 178. $C_8H_{12}O_4$. Calculated %: C 55.81; H 6.97; M 172.

After addition of two molecules of hydrogen the hydrogenation was broken off. The product was worked up to give a colorless liquid with b.p. 106-107° (10 mm).

n_D^{20} 1.4229; d_{20}^{20} 1.0559; MR_D 42.55; calculated 42.45.

4.411 mg substance: 8.855 mg CO_2. 3.172 mg H_2O. 4.353 mg substance: 8.760 mg CO_2; 3.100 mg H_2O. 0.2236 g substance; 18.00 g benzene: Δt 0.360°. Found %: C 55.78, 54.92; H 8.04, 7.97; M 174. $C_8H_{14}O_4$. Calculated %: C 55.17; H 8.04; M 177.2.

SUMMARY

1. Using 1,4-butynediol as an example, it was shown that a diprimary γ-acetylenic glycol in presence of colloidal palladium is hydrogenated more slowly than other γ-acetylenic glycols. No sharp slowing-down was observed after addition of two hydrogen atoms.

2. 1,4-Butynediol acetate has been synthesized for the first time. Its hydrogenation velocity in presence of palladium and platinum was investigated. 1,4-Butynediol acetate is found to hydrogenate more rapidly than

• 0.862 g substance; 0.736 g Pt; 50 ml ethyl alcohol; P 730 mm; T 21°; $2H_2$ = 506 ml.

•• 1.7 g substance; 0.736 g Pt; 50 ml ethyl alcohol; P 730 mm; T 21°; $2H_2$ = 524 ml.

1,4-butynediol. Hydrogenation proceeds at a uniform rate.

3. The products of hydrogenation of 1,4-butynediol acetate are described.

LITERATURE CITED

[1] Yu. S. Zalkind, J. Russ. Chem. Soc. 45, 1875 (1913); Yu. S. Zalkind, J. Gen. Chem. 5, 1733 (1935); Yu. S. Zalkind and K. Bystryakov, J. Russ. Chem. Soc., 47, 480 (1915); Yu. S. Zalkind and I. M. Gverdtsiteli, J. Gen. Chem. 9, 857 (1939); Yu. S. Zalkind and Kostyuchenko, J. Gen. Chem. 5, 1725 (1935); 7, 373 (1937); Yu. S. Zalkind and Neishtab, J. Russ. Chem. Soc. 50, 39 (1918); Yu. S. Zalkind and Bessonova, J. Russ. Chem. Soc. 53, 286 (1921); Yu. S. Zalkind, Moreva and Vishnyakova, J. Gen. Chem. 3, 94 (1933).

[2] Yu. S. Zalkind, J. Gen. Chem. 18, 2149 (1948).

[3] Lespieau, Comptes. rend. 150, 1761 (1910); Dupont, Comptes. rend. 156, 1623 (1913).

Received November 9, 1949

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144. HETEROCYCLIC COMPOUNDS. XX. STEREOISOMERISM IN THE HYDROGENATED THIOCHROMANONE SERIES. II.

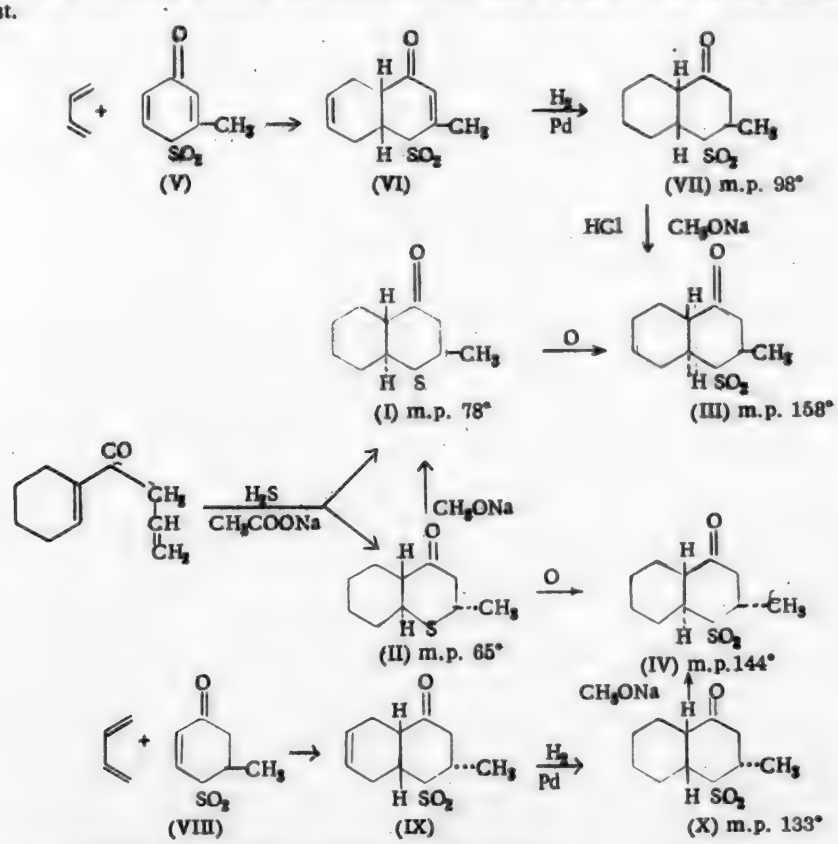
I. N. Nazarov, I. A. Gurvich and A. I. Kuznetsova

In a previous communication [1] we described a series of stereoisomers of hydrogenated derivatives of 2-methylthiochromanone, including three stereoisomeric bicyclic sulfones (III),(IV) and (VII).

In this investigation we synthesized a fourth and last stereoisomeric bicyclic sulfone (X). Consequently, all the possible stereoisomers of the dioxide of 2-methylhexahydro-1-thiochroman-4-one are now known and their structures have been established.

The previously obtained stereoisomeric bicyclic sulfones (III) and (IV) were synthesized by the action of hydrogen sulfide on allyl Δ^1-cyclohexenyl ketone in a weakly alkaline medium followed by oxidation of the stereoisomeric 2-methyl-hexahydro-1-thiochroman-4-ones (I) and (II) with potassium permanganate [2]. The third stereoisomeric bicyclic sulfone (VII) was obtained by condensation of the unsaturated monocyclic sulfone (V) with butadiene and subsequent reduction of the product of the diene synthesis (VI) in presence of Pd catalyst in a neutral medium.

The last stereoisomeric bicyclic sulfone (X) was obtained by condensation of butadiene with the unsaturated monocyclic sulfone (VII) followed by hydrogenation of the product of the diene synthesis (IX) in presence of Pd catalyst.



NOTE. The positions of the methyl groups are shown arbitrarily.

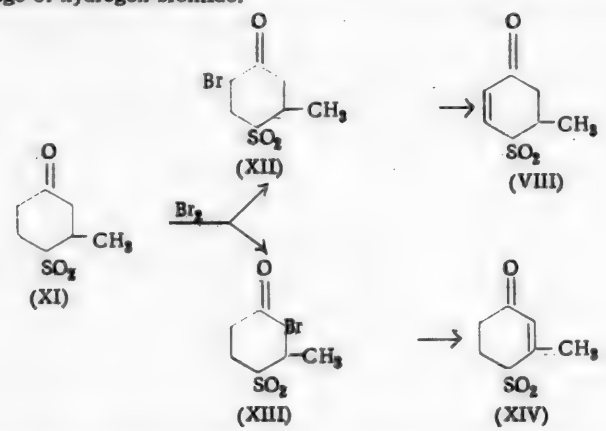
As was shown in the previous communication [1], the bicyclic sulfone (VII) isomerizes with extraordinary ease to the sulfone (III) under the influence of sodium methylate or hydrochloric acid. The bicyclic sulfone (X) also isomerizes to sulfone (IV) on boiling in dilute sodium methylate solution or on treating with hydrochloric acid.

The bicyclic sulfones (VII) and (X) possess a cis-configuration since they are obtained by the method of diene condensation, while the bicyclic sulfones (II) and (IV) belong, consequently, to the trans-series, as was confirmed by their preparation by isomerization of the cis-forms.

The bicyclic sulfones (VII) and (III), likewise (X) and (IV), are distinguished between themselves by the configuration at the junction of the rings, but they have the same spatial arrangement of the methyl groups at the second carbon atom. The 2-methylhexahydrothiochromanones (I) and (II) likewise differ from each other only in the arrangement of the methyl groups at the second carbon and are epimers.*

Hence the isomerization of the bicyclic sulfones (VII) and (X) proceeds at the angular hydrogen atom located in the α-position to the carbonyl group, and the previously described [2] isomerization of the thiochromanone (II) and the thiochromanone (I) in presence of sodium methylate is, consequently, an epimerization proceeding under the influence of the sulfide sulfur.

In one of the preceding papers we described the synthesis of the monocyclic unsaturated sulfone (V) and its condensation with butadiene [3]. Hydrogenation of the product of the diene synthesis (VI) under various conditions gives the bicyclic cis-sulfone (VII) or its trans-form (III). Consequently we were unable by this route to obtain the epimeric cis-sulfone (X). This sulfone was synthesized by condensation of butadiene with the unsaturated cyclic sulfone (VIII). The latter was prepared from the saturated sulfone (XI) by bromination followed by cleavage of hydrogen bromide.



Reaction of one molecule of bromine with the sulfone (XI) in glacial acetic acid, in presence of hydrogen bromide as catalyst, at 25-30° gives a mixture of the monobromides (XII) and (XIII) in a total yield of 80%.

When the reaction is performed without catalyst but with heating at 60°, a mixture of the isomeric monobromoketosulfones (XII) and (XIII) is obtained together with a small amount of dibromide in a total yield of up to 80%.

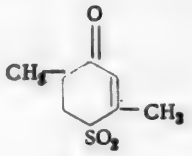
The unsaturated cyclic sulfones (VIII) and (XIV) were prepared by cleavage of hydrogen bromide from the bromoketosulfones (XII) and (XIII) by sodium acetate in boiling acetone.

Heating of sulfone (VIII) with butadiene in dioxan solution in a steel ampoule for 6 hours at 160-200° gave the bicyclic sulfone (IX) in 63% yield.

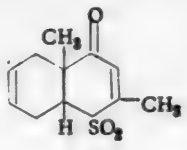
Sulfone (IX) is not isomerized by boiling in a dilute solution of sodium methylate, due to the stabilizing influence of the double bond in the ring. Hydrogenation of the product of the diene condensation (IX) with Pd catalyst in a neutral medium gives the saturated bicyclic cis-sulfone (X) which, as noted above, readily isomerizes to the trans-sulfone (IV) when heated with sodium methylate solution as well as under the action of hydrochloric acid.

* The term "epimers" is applied in the present instance to racemates.

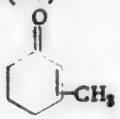
The unsaturated cyclic sulfone (XIV) completely fails to condense with butadiene at 175°, thus behaving like the previously described unsaturated cyclic sulfones (XV), (XVI) and (VI).



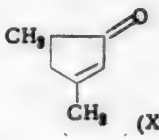
(XV)



(XVI)



(XVII)



(XVIII)

It is known that carbocyclic ketones of similar structure (XVII-XVIII) likewise do not undergo the diene synthesis [4,5]. Consequently substitution in the β-position to the carbonyl group greatly weakens the dienophilic properties of α,β-unsaturated cyclic ketones, just as is the case in the aliphatic series.

EXPERIMENTAL

The starting 2-methyltetrahydro-1-thiopyran-4-one (XI) was prepared by oxidation of 2-methyltetrahydro-1-thiopyran-4-one with potassium permanganate in acetone, as previously described [2,6].

5-Bromo-2-methyltetrahydro-1-thiopyran-4-one oxide (XII) and 3-bromo-2-methyltetrahydro-1-thiopyran-4-one (XIII). a) 5.6 g sulfone (XI) (m.p. 78-79°) was dissolved in 30 ml glacial acetic acid, and to the solution was added 1 ml of 4 N hydrogen bromide in glacial acetic acid. Under energetic stirring for 40 minutes, addition was made of 5.15 g bromine in 10 ml glacial acetic acid. The temperature of the solution was kept at 25-30°. Addition of the whole of the bromine was followed by separation of 4.8 g crystals; partial removal of the acetic acid in vacuum resulted in crystallization of another 1.9 g. In all, 6.7 g of mixed dibromides was obtained, or 80% of the theoretical yield.

4.8 g of the mixture of dibromides was recrystallized from methanol to give 2.4 g of crystals with m.p. 182-184°. Two recrystallizations from methanol gave pure 5-bromo-2-methyltetrahydro-1-thiopyran-4-one (XII) with m.p. 187.5-188°.

9.688 mg substance: 11.127 mg CO_2; 4.238 mg H_2O; 5.833 mg SO_4 + Br. 8.581 mg substance: 9.819 mg CO_2; 3.723 mg H_2O; 5.210 mg SO_4 + Br. Found %: C 31.34, 31.23; H 4.89, 4.85; S 11.04, 10.77; Br 27.49, 26.99. $C_6H_9O_3SBr \cdot 1.5\ CH_3OH$. Calculated %: C 31.15; H 5.23; S 11.09; Br 27.63.

Judging by the analysis, the substance contains methanol of crystallization which is not removed by prolonged drying of the bromide in the vacuum desiccator.

From the mother liquor after distillation of the methanol was separated 2.2 g crystals with m.p. 170-174° which was subjected to hydrogen bromide cleavage without further purification. In this way the unsaturated cyclic sulfone (XIV) was obtained, corresponding to 3-bromo-2-methyltetrahydro-1-thiopyran-4-one dioxide (XIII).

b) 6 g of the starting sulfone (XI) (m.p. 78-79°) was dissolved in 50 ml glacial acetic acid, and to the solution was added 5.5 g bromine. With energetic stirring the solution was heated to 61°. At this temperature instant decolorization of the solution occurred, followed by rapid darkening with temperature rise to 67°. (Further temperature rise was prevented by cooling with ice-water). Fractional crystallization yielded 7 g of crystals of the mixture of dibromides (XII) and (XIII), equivalent to 80% of theory. The first fraction (3 g) was the monobromide (XII), which was followed by a mixture of monobromosulfone and dibromosulfone (m.p. 160-164°). Cleavage of hydrogen bromide from this mixture led to separation of 2-methyl-1-thiopyran-4-one dioxide (V) (m.p. 139-140°), as well as a mixture of the unsaturated sulfones (VIII) and (XIV).

2-Methyl-2,3-dihydro-1-thiopyran-4-one (VIII). 3.2 g of the bromosulfone (XII) (m.p. 187-188°) was dissolved in 60 ml acetone and poured into a suspension of 2 g anhydrous sodium acetate in acetone. With

energetic stirring the mixture was heated for one hour on the water bath at 60-65°. After cooling, the solution was filtered, acidified with strong hydrochloric acid until decolorized, and again filtered. Removal of the solvent by distillation left 1.7 g crude crystals from which was obtained (recrystallization from alcohol) 1.35 g pure sulfone (VIII) in the form of lemon-colored crystals with m.p. 89.5-90°.

6.700 mg substance: 11.031 mg CO_2; 3.035 mg H_2O; 3.995 mg SO_4. 5.598 mg substance: 9.185 mg CO_2; 2.506 mg H_2O; 3.345 mg SO_4. Found %: C 44.93, 44.78; H 5.07, 5.01; S 19.90, 19.95. $C_6H_8O_3S$. Calculated %: C 44.98; H 5.03; S 20.02.

2-Methyl-5,6-dihydro-1-thiopyran-4-one (XIV). 2.2 g of the above-described mixture of bromides (m.p. 170-174°), containing the bromosulfone (XIII), was dissolved in 60 ml acetone, and the solution poured into a suspension of 1.6 g sodium acetate in 60 ml acetone, the mixture being then energetically stirred at 60-65° for one hour. Treatment as above yielded 0.65 g sulfone (XIV) with m.p. 115.6-116° (from alcohol).

5.200 mg substance: 8.580 mg CO_2; 2.257 mg H_2O. 6.798 mg substance: 11.195 mg CO_2; 2.994 mg H_2O. 5.460 mg substance: 9.018 mg CO_2; 2.403 mg H_2O; 3.320 mg SO_4. Found %: C 45.03, 44.94, 45.07; H 4.86, 4.93, 4.92; S 20.29. $C_6H_8O_3S$. Calculated %: C 44.98; H 5.03; S 20.02.

2-Methyl-5,8,9,10-tetrahydro-1-thiochroman-4-one (IX) 1.3 g sulfone (VIII) (m.p. 90°), 3 g butadiene, 15 ml dioxan and 0.01 g pyrogallol were heated in a steel ampoule for $5\frac{1}{2}$ hours at 200°. Removal of the solvent left 1.4 g of condensation product contaminated with polymer. After digestion in alcohol with animal charcoal and three recrystallizations from alcohol, the sulfone (IX) was obtained with m.p. 163-164.5° (yield 63%).

3.410 mg substance: 7.016 mg CO_2; 2.025 mg H_2O. 3.040 mg substance: 6.272 mg CO_2; 1.813 mg H_2O; 1.373 mg SO_4. Found %: C 56.17, 56.20; H 6.64, 6.67; S 15.08. $C_{10}H_{14}O_3S$. Calculated %: C 56.05; H 6.58; S 14.96.

The sulfone (IX) was obtained in a much purer form in an experiment under the same conditions but at 160°.

After boiling in dilute sodium methylate solution in methanol, the sulfone (IX) was recovered unchanged (no melting point depression in admixture with the original sulfone).

2-Methylhexahydro-1-thiochroman-4-one (X). 0.3 g sulfone (IX) (m.p. 163-164°) was hydrogenated with Pd catalyst• in 10 ml acetone. After an hour 35 ml hydrogen (18°, 750 mm) had been absorbed, or one molecule. After removal of solvent the substance melted without recrystallization at 131-132°. Recrystallization from alcohol yielded the cis-form (X) with m.p. 132.5-133°.

6.045 mg substance: 12.277 mg CO_2; 4.035 mg H_2O; 2.683 mg SO_4. 5.045 mg substance: 10.288 mg CO_2; 3.390 mg H_2O; 2.240 mg SO_4. Found %: C 55.42, 55.65; H 7.47, 7.52; S 14.82, 14.82. $C_{10}H_{16}O_3S$. Calculated %: C 55.53; H 7.46; S 14.83.

Isomerization of the cis-sulfone (X) into the trans-sulfone (IV). a) A solution of 0.15 g cis-sulfone (X) (m.p. 132-133°) in 2.5 ml methanol was boiled for $2\frac{1}{2}$ hours. After part distillation of the methanol in vacuum, 70 mg of a substance with m.p. 140-141° separated. After two recrystallizations from alcohol the substance melted at 142.5-143.5° and did not depress the melting point of the previously described trans-sulfone (IV).

b) 0.2 g cis-sulfone (X) (m.p. 132-133°) was dissolved in 5 ml 96% ethyl alcohol and to the solution was added two drops of strong hydrochloric acid. The solvent was evaporated and the resultant crystals were recrystallized from alcohol when they melted at 144-144.5°. No depression of m.p. of the trans-sulfone (IV).

Heating of sulfone (XIV) with butadiene. 0.65 g unsaturated sulfone (XIV) (m.p. 114-115°), 1.5 g butadiene, 7 ml dioxan and 0.02 g pyrogallol were heated in a steel ampoule for 5 hours at 175°. Removal of the solvent left 400 mg substance with m.p. 112-113° (from alcohol). A mixture with the original sulfone melted at 114-115°.

SUMMARY

1. Reaction of one molecule of bromine with a solution of sulfone (XI) in glacial acetic acid gives a mixture of the monobromosulfones (XII) and (XIII) in 80% yield.

• Palladium oxide on calcium carbonate.

2. Heating of the monobromosulfones (XII) and (XIII) with sodium acetate in acetone leads to cleavage of hydrogen bromide with formation of the corresponding unsaturated cyclic sulfones (VIII) and (XIV).

3. Condensation of sulfone (VIII) with butadiene at 160-200° gives the bicyclic sulfone (IX) in 63% yield.

4. Hydrogenation of sulfone (IX) in neutral medium with Pd catalyst yields the saturated bicyclic cis-sulfone (X), an epimer of the previously obtained cis-sulfone (VII).

5. In this manner, in addition to the previously prepared stereoisomeric sulfones (III), (IV), and (VII), a fourth and last stereoisomeric sulfone (X) has been synthesized by the diene condensation.

6. The cis-sulfone (X) readily isomerizes to the trans-form (IV) in presence of sodium methylate.

7. The unsaturated sulfone (XIV), like the previously described sulfones (VI), (XV) and (XVI), does not undergo the diene condensation with butadiene at temperatures up to 200°.

LITERATURE CITED

[1] I. N. Nazarov, I. A. Gurvich and A. I. Kuznetsova, J. Gen. Chem. 22, 1236 (1952).*

[2] I. N. Nazarov, A. I. Kuznetsova and I. A. Gurvich, J. Gen. Chem. 19, 2148 (1949).**

[3] I. N. Nazarov, I. A. Gurvich and A. I. Kuznetsova, J. Gen. Chem. 22, 990 (1952).***

[4] R. Robinson, J. Walker, J. Chem. Soc., 1935, 1530.

[5] I. N. Nazarov and T. D. Nagibina, J. Gen. Chem. 20, 531 (1950).****

[6] I. N. Nazarov, I. A. Gurvich and A. I. Kuznetsova, J. Gen. Chem. 22, 984 (1952).*****

Received December 19, 1950

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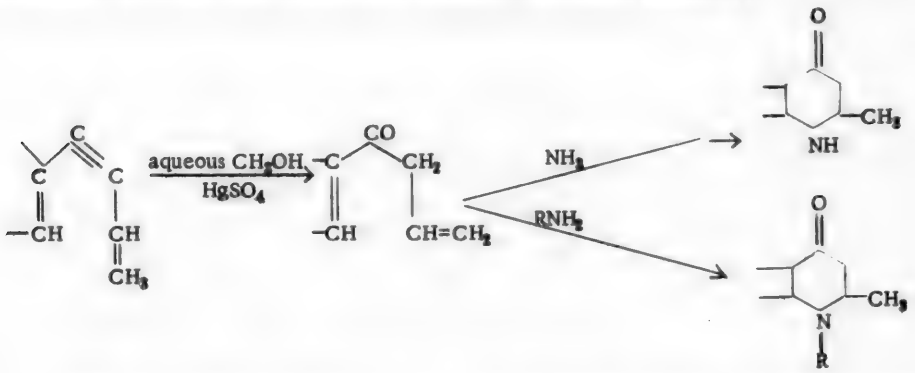
*See Consultants Bureau translation, p. 1283.
**See Consultants Bureau translation, p. a-621.
***See Consultants Bureau translation, p. 1045.
****See Consultants Bureau translation, p. 561.
*****See Consultants Bureau translation, p. 1039.

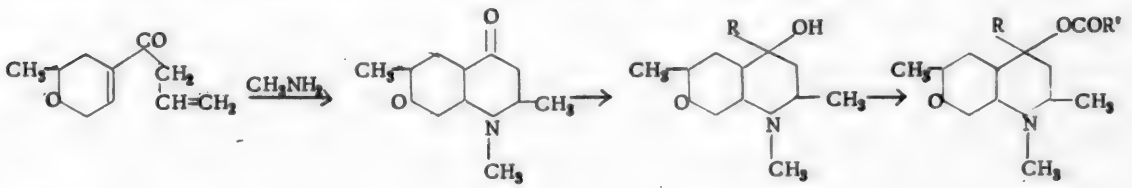
145. HETEROCYCLIC COMPOUNDS. XXI. SYNTHESIS AND TRANSFORMATIONS OF 1,2,6,6-TETRAMETHYL-7-OXA-4-KETODECAHYDROQUINOLINE

I. N. Nazarov and S. A. Vartanyan

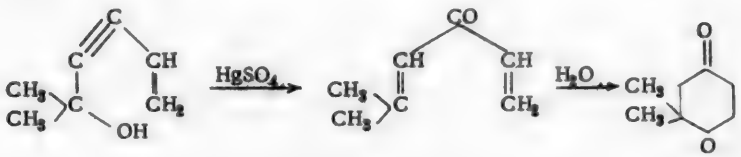
A few years ago we discovered in our laboratory a simple method of preparation of various gamma-piperidones, based upon the hydration of dienynes to the corresponding dienones (vinylallyl ketones) [1] and cyclization of the latter under the action of ammonia and primary amines [2]:



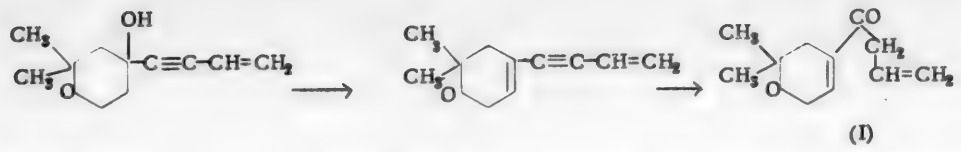
Using this method for preparation of ....γ-piperidones, we recently synthesized 1,2,6-trimethyl-7-oxa-4-decahydroquinoline and obtained a series of the alcohols and esters corresponding thereto [3]:



In the present paper the synthesis is described of two new representatives of the bicyclic pyranopiperidones (II) and (III), starting from 2,2-dimethyltetrahydro-4-pyrone which is easily prepared from the technically available dimethylvinylethinyl carbinol [4]:



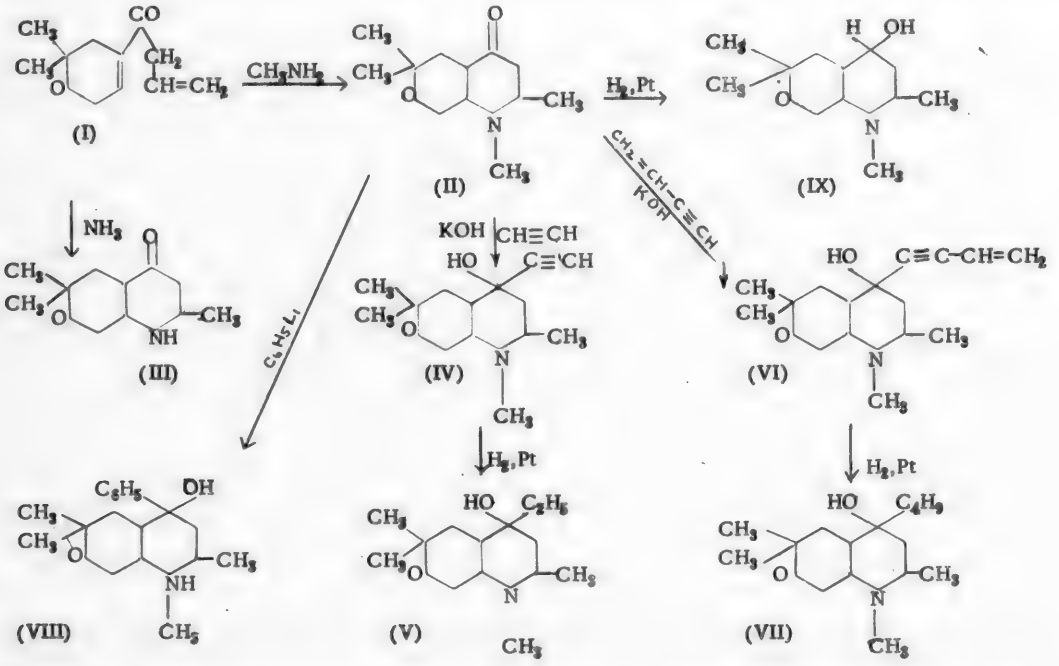
As was shown in an earlier communication, 2,2-dimethyltetrahydro-4-pyrone condenses with vinylacetylene to give 2,2-dimethyl-4-vinylethinyltetrahydro-4-pyranol which dehydrates to the corresponding pyrano diene; hydration of the latter in aqueous methanol solution then results in a high yield of the pyrano dienone (I) [5]:



(I)

Like other vinylallyl ketones, the pyranic dienone (I) readily reacts with ammonia and methylamine to form in good yield, respectively, 2,6,6-trimethyl-7-oxa-4-ketodecahydroquinoline (III) and 1,2,6,6-tetramethyl-7-oxa-4-ketodecahydroquinoline (II).

These compounds are of interest as starting materials for the synthesis of various heterocyclic compounds containing both the piperidine and the tetrahydropyran ring. Under the influences of powdered potassium hydroxide the bicyclic pyranopiperidine (II) readily condenses with acetylene and gives, in a yield of about 70%, 1,2,6,6-tetramethyl-7-oxa-4-ethinyl-4-hydroxy decahydroquinoline (IV), which takes up two molecules of hydrogen when hydrogenated in presence of Pt catalyst and forms 1,2,6,6-tetramethyl-7-oxa-4-ethyl-4-hydroxy-decahydroquinoline (V):



Under the influence of potassium hydroxide the piperidone (II) likewise readily condenses with vinylacetylene [6] and gives a good yield of 1,2,6,6-tetramethyl-7-oxa-4-vinylethinyl-4-hydroxy decahydroquinoline (VI) which absorbs three molecules of hydrogen when hydrogenated in presence of Pt catalyst and is converted into 1,2,6,6-tetramethyl-7-oxa-4-butyl-4-hydroxy decahydroquinoline (VII). Reaction of phenyllithium [7] with the bicyclic pyranopiperidone (II) results in a good yield of 1,2,6,6-tetramethyl-7-oxa-4-phenyl-4-hydroxy-decahydroquinoline (VIII). Catalytic hydrogenation of the bicyclic pyranopiperidone (II) in presence of Pt catalyst leads to 1,2,6,6-tetramethyl-7-oxa-4-hydroxydecahydroquinoline (IX).

All of the alcohols of the 7-oxadecahydroquinoline series (IV, V, VI, VII, VIII, and IX) described in this paper were obtained in the form of a mixture of stereoisomers whose separation presents great difficulties, due to the hygroscopicity of the hydrochlorides and their failure to recrystallize. Attempts to prepare esters of these alcohols by acylation with the help of benzoyl chloride, acetyl chloride and propionic anhydride were also unsuccessful. Under mild conditions the hydrochloride of the original piperidol separated in all cases, and under drastic conditions the product resinifies.

EXPERIMENTAL

The starting allyl-2,2-dimethyl-Δ^4-dihydro-4-pyranyl ketone (I) was prepared by the previously described method and had the constants: b.p. 94-96° at 2mm; n_D^{20} 1.4873 [5].

Preparation of 2,6,6-trimethyl-7-oxa-4-ketodecahydroquinoline (III). A mixture of 12 g ketone (I), 100 g aqueous ammonia (s.g. 0.9) and 15 ml methyl alcohol was shaken for 20 minutes until a homogeneous solution was obtained, and then saturated with ammonia at −2° (weight increase 30 g) and heated in a sealed metal cylinder at 80° for $3\frac{1}{2}$ hours. The ammonia was removed in vacuum, at first in the cold and then on a water bath at 45°. The solution was neutralized with hydrochloric acid until weakly acid and the neutral products were extracted with ether, but only a trace was found.

The organic base was salted out with potassium carbonate, extracted with ether, dried with sodium sulfate and distilled in vacuum to give 8.6 g piperidone (III) in the form of a mobile liquid which turned yellow on standing and had a characteristic ammoniacal odor; b.p. 128-130° at 6 mm.

n_D^{20} 1.4911; d_4^{20} 1.0625; MR_D 53.56; calculated 53.90.

7.262 mg substance: 17.850 mg CO_2; 6.350 mg H_2O. 3.595 mg substance: 8.870 mg CO_2; 3.200 mg H_2O. Found %: C 67.08, 67.33; H 9.78, 9.96. $C_{11}H_{19}O_2N$. Calculated %: C 67.00; H 9.64.

The 2,4-dinitrophenylhydrazone of piperidone (III) melts at 210-212° (after recrystallization from alcohol).

Preparation of 1,2,6,6-tetramethyl-7-oxa-4-ketodecahydroquinoline (II). A mixture of 60 g ketone (I) and 70 g 35% aqueous methylamine solution was shaken for a few minutes until a transparent solution was formed (during this operation the temperature rose to 43°). The mixture was then heated in a metallic ampoule at 70° in the course of 1.5 hours. The excess of methylamine was distilled off at 45° in a 75 mm vacuum. The solution was neutralized with hydrochloric acid until weakly acid, and the neutral products extracted with ether, but only a trace was found. The organic base was salted out with sodium hydroxide, extracted with ether, dried with sodium sulfate and fractionated in vacuum to give 58.3 g of piperidone (II) in the form of a liquid which turned yellow on standing and had a characteristic ammoniacal odor; b.p. 113-114° at 2mm.

n_D^{20} 1.4973; d_4^{20} 1.0690; MR_D 59.35; calculated 58.80.

13.48 mg substance: 12.23 mg H_2O; 33.73 mg CO_2. 12.23 mg substance: 11.20 mg H_2O; 30.56 mg CO_2. Found %: C 68.29, 68.19; H 10.15, 10.25. $C_{12}H_{21}O_2N$. Calculated %: C 68.24, H 9.99.

The picrate was prepared by mixing piperidone (II) with saturated alcoholic solution of picric acid. On heating in alcohol it dissolves readily and only comes down after distilling off the greater part of the solvent; it is then in the form of a dark-brown, fine powder with m.p. 162-164°.

5.622 mg substance: 0.616 ml N_2 (24°, 736 mm). 5.920 mg substance: 0.643 ml N_2 (22°, 743 mm). Found %: N 12.33, 12.20. $C_{18}H_{24}O_9N_4$. Calculated %: N 12.72.

Hydrogenation of 1,2,6,6-tetramethyl-7-oxa-4-ketodecahydroquinoline (II). 3.2 g freshly distilled piperidone (II) was hydrogenated in 15 ml ethyl alcohol in presence of Pt catalyst. 360 ml hydrogen was absorbed. Complete hydrogenation of the carbonyl group requires 370 ml hydrogen. Hydrogenation was completed in 2 hours. 1.8 g 1,2,6,6-tetramethyl-7-oxa-4-hydroxydecahydroquinoline (IX) was obtained in the form of a transparent, viscous liquid with a characteristic odor; b.p. 121-122.5° at 2 mm. The product crystallized when petrol (b.p. 45-60°) was added; it was isolated in the form of a white powder with m.p. 131-134°.

12.47 mg substance: 31.08 mg CO_2, 12.19 mg H_2O. 12.28 mg substance: 30 65 mg CO_2; 12.04 mg H_2O. Found%: C 68.02, 68.11; H 10.94, 10.72. $C_{12}H_{23}O_2N$. Calculated %: C 67.60; H 10.80.

The hydrochloride of base (IX) is an amorphous mass which deliquesces on standing in the air.

Synthesis of 1,2,6,6-tetramethyl-7-oxa-4-ethinyl-4-hydroxydecahydroquinoline (IV). Into a three-necked flask fitted with a mechanical stirrer, a dropping funnel and a reflux condenser were introduced 9.4 g powdered potassium hydroxide and 150 ml dry ether. At a temperature of −2° this mixture was saturated with acetylene in the course of 30 minutes. Addition was then made with continuous stirring in a stream of acetylene of 20 g piperidone (IV) dissolved in an equal volume of ether. After the piperidone had been added, the acetylene stream was continued for a further 4 hours at −2° and 2 hours at room temperature. The potassium hydroxide was washed

out with water (10 ml), carbon dioxide was passed through the ether solution for complete removal of the alkali, and the product was dried with sodium sulfate and distilled in vacuum. 16.5 g of the acetylenic alcohol (IV) was obtained in the form of a very viscous, yellow liquid, b.p.137-139° at 2 mm. It solidified to a vitrous mass in the receiver.

10.53 mg substance: 9.28 mg H_2O; 27.46 mg CO_2. 9.53 mg substance: 8.43 mg H_2O; 24.74 mg CO_2. Found %: C 71.17, 70.85; H 9.87, 9.86. $C_{14}H_{23}O_2N$. Calculated %: C 70.87; H 9.7.

The hydrochloride of the acetylenic alcohol (IV), after drying in a vacuum desiccator over phosphorus pentoxide, melts at 116-120°. It is a hygroscopic, amorphous white powder which deliquesces when stored in contact with air; on recrystallization it comes down in the form of a noncrystalline, amorphous mass.

Hydrogenation of 1,2,6,6-tetramethyl-7-oxa-4-ethinyl-4-hydroxydecahydroquinoline (IV). 3 g of freshly distilled acetylenic alcohol (IV) was hydrogenated in 15 ml alcohol in presence of Pt catalyst, 523 ml hydrogen being absorbed. Complete hydrogenation of the acetylenic alcohol requires 600 ml hydrogen. 2.4 g of 1,2,6,6-tetramethyl-7-oxa-4-ethyl-4-hydroxydecahydroquinoline (V) was obtained in the form of a transparent, viscous liquid with a characteristic odor; b.p. 113-115° at 1 mm.

8.597 mg substance: 21.675 mg CO_2; 8 410 mg H_2O. 4.440 mg substance: 11.215 mg CO_2; 4.350 mg. H_2O. Found %: C 68.81, 68.93; H 10 95, 10.96. $C_{14}H_{27}O_2N$. Calculated %: C 69.70; H 11.24.

The hydrochloride of the ethylpiperidol (V) is a viscous mass which does not crystallize.

Synthesis of 1,2,6,6-tetramethyl-7-oxa-4-vinylethinyl-4-hydroxydecahydroquinoline (VI). Into a round-bottomed flask fitted with a mechanical stirrer, a mercury seal and a dropping funnel was introduced 8.4 g powdered potassium hydroxide and 100 ml dry ether. To this mixture, cooled to −2°, was added in small portions with vigorous stirring 10 g vinyl acetylene and 20 g piperidone (II) dissolved in 50 ml dry ether. After the addition of the ether solution of vinylacetylene and piperidone (II), stirring was continued for a further eight hours while being cooled with ice-water, and the reaction mass left overnight. On the next day the mixture was stirred for a further two hours, treated with water (10 ml), and a stream of carbon dioxide passed through the ether layer for complete removal of alkali. The product was then dried with sodium sulfate and distilled in vacuum to give 19.3 g of the vinylacetylenic alcohol (VI); b.p. 150-152° at 1 mm.

15.13 mg substance: 40.37 mg CO_2; 13.06 mg H_2O. 9.63 mg substance: 25.78 mg CO_2; 8.47 mg H_2O. Found %: C 72.83, 73.06; H 9.67, 9.84. $C_{16}H_{25}O_2N$. Calculated %: C 73.01; H 9.58.

This alcohol is a yellowish glassy product which softens on heating. Its hydrochloride is a white hygroscopic powder melting at 120-124°.

Hydrogenation of 1,2,6,6-tetramethyl-7-oxa-4-vinylethinyl-4-hydroxydecahydroquinoline (VI). 3 g freshly distilled material (VI) was hydrogenated in solution in 15 ml alcohol in presence of Pt catalyst. 813 ml hydrogen was absorbed as compared with the theoretical requirement of 822 ml. The catalyst was filtered off, the alcohol distilled off, and the residue fractionated in vacuum to give 2.6 g of the butylpiperidol (VII) as a transparent, viscous liquid with a characteristic odor, b.p. 140-143° (2 mm). This product was a mixture of the two isomers of 1,2,6,6-tetramethyl-7-oxa-4-butyl-4-hydroxydecahydroquinoline. Dilution with ether resulted in crystallization of about 1 g of pure substance which melted at 114-116° (from ether) and was readily soluble in petrol (b.p. 65-78°), acetone and benzene.

4.872 mg substance: 12.742 mg CO_2; 5.105 mg H_2O. 5.673 mg substance: 14.878 mg CO_2; 5.910 mg H_2O. Found %: C 71.37, 71.57; H 11.72, 11.66. $C_{16}H_{31}O_2N$. Calculated %: C 71.37; H 11.52.

The hydrochloride of this alcohol melted at 109-112° after drying in a vacuum desiccator over phosphorous pentoxide. It was a hygroscopic, white amorphous powder which deliquesced in the air and on recrystallization separated in the form of a viscous, noncrystalline mass.

The residue following removal of the crystalline isomer of (VII) was distilled in vacuum to give 1.7 g of a mixture of the isomeric alcohols (VII) with b.p. 140-142° at 2 mm and consisting of a vitreous mass which softened on heating.

4.021 mg substance: 10.480 mg CO_2; 4.120 mg H_2O. 6.005 mg substance: 15.620 mg CO_2; 6.165 mg H_2O. Found %: C 71.13, 70.98; H 11.47, 11.49. $C_{16}H_{31}O_2N$. Calculated %: C 71.37; H 11.52.

The hydrochloride of this mixture melted at 120-123°.

Synthesis of 1,2,6,6-tetramethyl-7-oxa-4-phenyl-4-hydroxydecahydroquinoline (VIII). The following reaction was conducted in a nitrogen atmosphere. Into a three-necked round-bottom flask, fitted with a mechanical stirrer, mercury seal, dropping funnel, a tube for nitrogen and a thermometer, was introduced 50 ml absolute ether, 1 g small lithium turnings and 4 g bromobenzene.

After the reaction had commenced, gradual addition was made of a further 14 g bromobenzene dissolved in the same volume of absolute ether. There was then added to the mixture 50 ml ether, and the reaction mass stirred at room temperature for one hour and then at the temperature of boiling ether for 30 minutes. Dropwise addition was then made at a temperature of −12° to the so-prepared phenyllithium of 9 g of the piperidone (II) dissolved in 10 ml absolute ether. On the following day the mixture was heated for two hours at the temperature of boiling ether, and the reaction product was hydrolyzed with 12 ml of water at a temperature of −6°. The ether layer was separated, and the aqueous layer was extracted with three portions of ether, saturated with potassium carbonate, and extracted once more with ether. The ether extracts were combined, and dried with sodium sulfate, the ether was distilled off, and the product distilled in vacuum giving 9.2 g of the phenylpiperidol (VIII). The latter was a very viscous, yellowish liquid boiling at 163° (1 mm).

4.036 mg substance: 11.092 mg CO_2; 3.340 mg H_2O. 3.995 mg substance: 10.985 mg CO_2, 3.352 mg H_2O. Found %: C 75.00, 75.04; H 9.26, 9.39. $C_{18}H_{27}O_2N$. Calculated %: C 74.74; H 9.3. 0.063 g substance: 4.17 ml CH_4 (19°, 738 mm). 0.080 g substance: 5.3 ml CH_4 (20°, 739 mm). Found %: active hydrogen 0.29, 0.30. Calculated %: active hydrogen 0.34.

On cooling the product solidified to a vitreous mass which was converted by grinding into an amorphous powder. The hydrochloride of this alcohol melted at 185-187° after drying in the vacuum desiccator over phosphorous pentoxide. It behaves like the hydrochloride of the above-described piperidols.

Attempt to prepare the benzoate of 1,2,6,6-tetramethyl-7-oxa-4-phenyl-4-hydroxydecahydroquinoline (XI). To phenyllithium prepared, as described above, from 1 g of small pieces of metallic lithium and 15 g bromobenzene in 50 ml absolute ether was added dropwise 9 g of the piperidone (II) dissolved in the same volume of ether. Mixing was effected for 2 hours at room temperature and 2 hours at the boiling point of ether. There was added to the resultant complex at −5°, dropwise, 10 ml of benzoyl chloride dissolved in 10 ml absolute ether. The mixture was stirred for one hour at 20° and for 3 hours at the boiling point of ether before being left overnight. On the following day there was added 20 ml of water to the reaction mass, the aqueous layer was saturated with sodium carbonate and extracted with ether; the product was dried with sodium sulfate and distilled in vacuum. There was isolated 3.2 g of the above-described phenylpiperidol (VIII) with b.p. 160-164° (1 mm); m.p. of hydrochloride 176-180°. Consequently no benzoylation had taken place under the described conditions.

SUMMARY

Reaction of methylamine and ammonia with the dienone (I) gives, in good yield, the bicyclic γ-piperidones (II and III) containing the condensed tetrahydropyran ring.

Condensation of the bicyclic pyranopiperidone (II) with acetylene and vinylacetylene results in formation in good yield of the acetylenic and vinylacetylenic piperidols (IV and VI).

The phenylpiperidol (VIII) is obtained in good yield by the action of phenyllithium on the bicyclic pyranopiperidone (II).

All the above-described unsaturated compounds were hydrogenated in presence of Pt catalyst to give the corresponding saturated compounds.

LITERATURE CITED

[1] I. N. Nazarov and I. I. Zaretskaya, Bull. Acad. Sd. USSR, Div. Chem. Sci. 1, 211 (1941).

[2] I. N. Nazarov and V. A. Rudenko, Bull. Acad. Sci. USSR, Div. Chem. Sci., 6, 610 (1948).

[3] I. N. Nazarov and S. A. Vartanyan, J. Gen. Chem. 21, 374 (1951); see Consultants Bureau translation, p.413.

[4] I. N. Nazarov and co-workers, Bull. Acad. Sci. USSR, Div. Chem. Sci. 223 (1940); 50 (1943).

[5] I. N. Nazarov and I. V. Torgov, J. Gen. Chem., 18, 1338 (1948).

[6] I. N. Nazarov and V. Ya. Raigorodskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 6, 631 (1948); I. N. Nazarov, V. Ya. Raigorodskaya and V. A. Rudenko, ibid, 1, 68 (1949).

[7] Lee, Ziering and co-workers, J. Org. Chem. 12, 885 (1947).

Received December 19, 1950

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INVESTIGATION OF THE ACTION OF BROMINE ON α,α-(p-DIMETHYLAMINOPHENYL)-β-PHENYLETHYLENE

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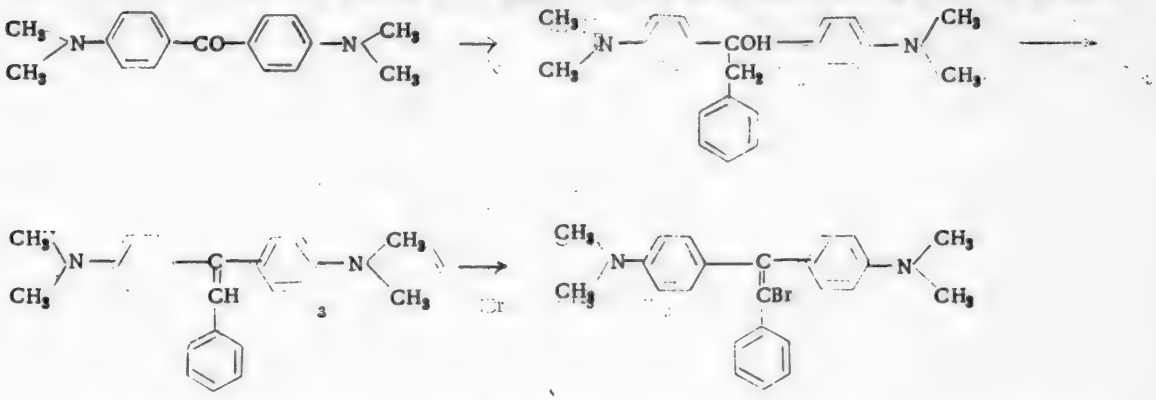
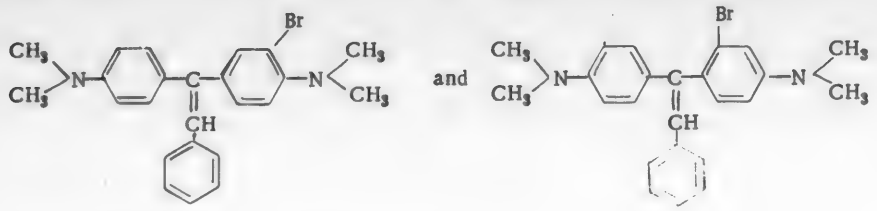
With the objective of studying the action of bromine on triphenylethylene derivatives, we have investigated the behavior of this halogen towards α,α-di-(p-dimethylaminophenyl)-β-phenylethylene. The possibilities arising in the action of bromine on α,α-di-(p-dimethylaminophenyl)-β-phenylethylene are replacement of the hydrogen of the ethylene group by bromine, addition of two atoms of bromine, or substitution of the hydrogen of the benzene ring.

Taking into consideration the stability of the halogen at a double bond, the formation of α,α-di-(p-dimethylaminophenyl)-β-phenyl-β-bromoethylene appeared probable. The synthesis of the latter was of interest in connection with its similarity to triphenylbromoethylene whose estrogenic properties have been described in the literature [1].

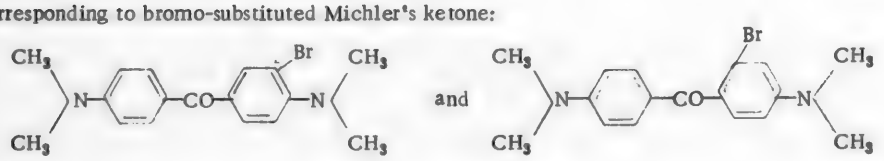
For the synthesis of α,α-di-(p-dimethylaminophenyl)-β-phenyl-β-bromoethylene we started from α,α-di-(p-dimethylaminophenyl)-β-phenylethylene, which was prepared by dehydration of α,α-di-(p-dimethylaminophenyl)-benzyl carbinol. The latter was prepared by the Grignard reaction from Michler's ketone and benzyl chloride:



Reaction of benzyl magnesium chloride with Michler's ketone gave α,α-di-(p-dimethylaminophenyl)-β-phenylethylene together with a small amount of α,α-di-(p-dimethylaminophenyl)-benzyl carbinol, which suggests dehydration of the latter in the course of the reaction. Oxidation of α,α-di-(p-dimethylaminophenyl)-β-phenylethylene with potassium permanganate yielded Michler's ketone; the presence of benzaldehyde was detected by its odor. Bromination of α,α-di-(p-dimethylaminophenyl)-β-phenylethylene with bromine in chloroform led to separation of two products: One of these had a blue color and preponderated; it melted at 151-154°; the other was green and melted at 169-170°. Analysis showed them to be isomers since they both had the composition $C_{24}H_{25}N_2Br$ and contained one atom of bromine. The bromine-containing compounds were oxidized with potassium permanganate (in acetone solution); a substance was obtained which melted at 122-124° and contained halogen; among the oxidation products was benzaldehyde. Since these data clearly indicated that the action of bromine on α,α-di-(p-dimethylaminophenyl)-β-phenylethylene does not result in addition of bromine nor in substitution of hydrogen at the ethylene bond, the only possible conclusion was that bromine replaces hydrogen in the aromatic nucleus. To test this conclusion, Michler's ketone was subjected to bromination when a monobromo derivative with m.p. 118-127° was obtained and was found to be identical with the bromo derivative isolated after oxidation of the bromo-substituted α,α-di-(p-dimethylaminophenyl)-β-phenylethylene. On the basis of these data we can conclude that in the bromination of α,α-di-(p-dimethylaminophenyl)-β-phenylethylene there are formed bromo-substituted derivatives to which the following structure may be attributed:



corresponding to bromo-substituted Michler's ketone:



EXPERIMENTAL

α,α-Di-(p-dimethylaminophenyl)-benzyl carbinol. 53.6 g Michler's ketone, dissolved in benzene, was gradually added to benzyl magnesium chloride in ether. The Grignard reagent was prepared from 4.8 g magnesium and 25.2 g benzyl chloride (b.p. 179°). Heat was developed during the reaction with the ketone. The color of the mixture first turned green and later brown. After the whole of the ketone had been added, the mixture was heated on the water bath with stirring for 3 hours. The reaction product was decomposed with ice-water and acidified with dilute hydrochloric acid until the basic salts of magnesium had gone into solution; three layers were formed. The top one had the consistency of a slurry; the middle one (ether-benzene) had a green color; the bottom one was an aqueous solution. The solid material was separated at the pump and the ether-benzene layer was collected through a separating funnel. The aqueous layer was washed with benzene and the extract combined with the ether-benzene solution. Distillation of the ether and benzene left 25 g of substance which, after recrystallization from alcohol, proved to be identical with the product from the solid mass; in all there was 37 g of product (55% yield based on the Michler ketone). After recrystallization from alcohol or chloroform the product melted at 127-128° and consisted of light-yellow crystals which were insoluble in water, soluble in hot alcohol, chloroform and benzene. We could not confirm the observation of Madelung and Volker [2] that on recrystallization from alcohol part of the product does not dissolve in the alcohol and crystallizes from benzene with m.p. 173°. It is true that on recrystallization from alcohol a residue is obtained which is poorly soluble in alcohol and easily soluble in benzene, but this substance likewise melts at 127-128°. The most appropriate solvent for crystallization of the product was found to be a mixture of equal parts of alcohol and benzene.

From the acid aqueous solution was separated 2.5 g of a substance in the form of bright needles with a greenish tinge, m.p. 187-189°. According to the analytical data these corresponded to α,α-di(p-dimethylaminophenyl)-benzyl carbinol . The product melting at 127-128° appeared, judging by the analysis, to be α, α-di-(p-dimethylaminophenyl)-β-phenylethylene.

In general the obtained results are consistent with those of other workers [3] who brought Michler's ketone into reaction with various organomagnesium compounds and obtained not tertiary alcohols but products of their dehydration. Attention may be drawn to the fact that it is more expedient to use a deficiency of ketone in relation to the benzyl chloride (not more than 60% of the theoretical) since it is rather difficult to eliminate unreacted ketone.

Analysis of α,α-di-(p-dimethylaminophenyl)-benzyl carbinol.

0.1186 g substance: 7.60 ml N_2 (21°, 768 mm). 0.0988 g substance: 6.60 ml N_2 (18°, 745 mm). Found %: N 7.51, 7.69. $C_{24}H_{28}ON_2$. Calculated %: N 8.77.

Analysis of α,α-di-(p-dimethylaminophenyl)-β-phenylethylene.

0.0902 g substance: 6.20 ml N_2 (20°, 776 mm). 0.0824 g substance: 5.70 ml N_2 (19°, 774 mm). Found %: N 8.11, 8.19. $C_{24}H_{26}N_2$. Calculated %: N 8.18.

Oxidation of α,α-di-(p-dimethylaminophenyl)-β-phenylethylene. 3.42 g α,α-di-(p-dimethylaminophenyl)-

β-phenylethylene was dissolved in 50 ml acetone and oxidized with 126.4 ml 1% potassium permangante solution for 2 hours with stirring. After distillation of the acetone, the residue was filtered, washed with hot water and treated with hot benzene. The benzene was driven off to leave 1.6 g of a greenish substance, melting (after recrystallization from alcohol) at 170-172° and not depressing the melting point of Michler's ketone. The aqueous liquid had a strong odor of benzaldehyde. The formation of Michler's ketone and benzaldehyde on oxidation demonstrates that the compound has the structure of α,α-di-(p-dimethylaminophenyl)-β-phenylethylene.

Bromination of α,α-di-(p-dimethylaminophenyl)-β-phenylethylene. 171.1 g α,α-di-(p-dimethylaminophenyl)-β-phenylethylene was dissolved in 85 ml chloroform, and to the solution, with stirring, was gradually added a solution of 8 g bromine in 25 ml chloroform. Heat was developed during this addition and the color changed from light-green to blue with a greenish tinge. After removing the chloroform, there remained a viscous, blue mass which slowly crystallized. On recrystallization from alcohol it was found to be heterogeneous; the greater part had a blue color and melted at 151-154°; its amount was 14.2 g; a subsequent series of recrystallizations from benzene yielded 5.1 g substance with m.p. 169-170°; the color of this was light-green. The total yield was thus 19.3 g or 68% of theory.

Analysis of the bromide with m.p. 151-154°.

0.1496 g substance: 8.60 ml N_2 (18°, 760 mm). 0.1733 g substance: 10.20 ml N_2 (17°, 770 mm). 0.4700 g substance: 10.75 ml 0.1 N $AgNO_3$ (by Stepanov's method). 0.4372 g substance: 10.10 ml 0.1 N $AgNO_3$. Found %: N 6.74, 6.81; Br 18.24, 18.47. $C_{24}H_{25}N_2Br$. Calculated%: N 6.65; Br 19.00

Oxidation of the bromide melting at 151-154°. 4.2 g of the bromide was dissolved in 50 ml acetone and the solution oxidized with 126 ml of 1% solution of potassium permanganate. The precipitate formed after driving off the acetone was filtered and washed with hot water; the aqueous liquid had the odor of benzaldehyde and gave a negative reaction for bromine. The precipitate was worked up with hot benzene and ether. After distilling off the solvents there remained a yellow mass which after recrystallization melted at 122-124°. Yield 2.04 g. No reaction for halogen.

0.1098 g substance: 7.8 ml N_2 (16°, 770 mm). 0.1248 g substance: 8.7 ml N_2 (18°, 772 mm). Found %: N 8.50, 8.28. $C_{17}H_{19}ON_2Br$. Calculated %: N 8.04. 0.2007 g substance: 5.05 ml 0.1 N $AgNO_3$. 0.2218 g substance: 5.95 ml 0.1 N $AgNO_3$. Found %: Br 20.12, 21.42. $C_{17}H_{19}ON_2Br$. Calculated %: Br 23.00.

An attempt to prepare the semicarbazone of the bromo ketone was unsuccessful.

Analysis of the bromide with m.p. 169-170°.

0.1495 g substance: 8.80 ml N_2 (18°, 770 mm). 0.1620 g substance: 9.40 ml N_2 (18°, 766 mm). Found %: N 6.99, 6.86. $C_{24}H_{25}N_2Br$. Calculated %: N 6.65. 0.4824 g substance: 11.00 ml 0.1 N $AgNO_3$ (by Stepanov's method). 0.4538 g substance: 10.80 ml 0 1 N $AgNO_3$. Found %: Br 18.26, 19.02. $C_{24}H_{25}N_2Br$. Calculated %: Br 19.00.

Oxidation of the bromide with m.p. 169-170°. This was effected, as above, with 1% potassium permanganate solution. The bromo ketone had a yellow color, somewhat paler than previously, and melted after recrystallization from benzene at 166-167°. The aqueous alkaline liquid gave off the odor of benzaldehyde and gave a negative reaction for bromine. The following results were obtained in nitrogen determinations (Dumas) and bromine determinations (Pirn and Schiff):

0.1194 g substance: 7.80 ml N_2 (15°, 770 mm). 0.0807 g substance: 5.30 ml N_2 (16°, 770 mm). 0.2090 g substance: 5.80 ml 0.1N $AgNO_3$. 0.2326 g substance: 6.70 ml 0.1 N $AgNO_3$. Found %: N 7.84, 7.86; Br 22.12, 23.02. $C_{17}H_{19}ON_2Br$. Calculated %: N 8.04; Br 23.00.

An attempt to prepare the semicarbazone of the bromo ketone was unsuccessful.

Bromination of Michler's ketone. 2.68 g Michler's ketone was dissolved in 50 ml chloroform, and to the solution was gradually added a solution of 1.6 g bromine in 15 ml chloroform. After driving off the chloroform and recrystallizing from alcohol and benzene there was obtained 2.5 g of a substance with a gradual melting point of 117-128°; it was evidently a mixture of the isomeric monobromo derivatives of the ketone whose separation was attended with difficulties.

SUMMARY

1. Reaction of benzyl magnesium chloride with Michler's ketone gives mainly α,α-di-(p-dimethylaminophenyl)-β-phenylethylene together with a smaller amount of α,α-di-(p-dimethylaminophenyl)-benzyl carbinol.

2. In the reaction of bromine with α,α-di-(p-dimethylaminophenyl)-β-phenylethylene the bromine replaces a hydrogen of the aromatic nucleus with formation of isomeric bromo derivatives of α,α-di-(p-dimethylaminophenyl)-β-phenylethylene.

3. A monobromo-substituted ketone is formed by the action of bromine on Michler's ketone

LITERATURE CITED

[1] F. W. Schueler, Science, 103, 221 (1946).

[2] W. Madelung and F. Volker, Chem. Zentr., I, 2072 (1927).

[3] Freund and Majer, Ber., 39, 1118 (1906).

Received October 19, 1950

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SYNTHESIS OF 3,4-BENZPHENANTHRENE AND ITS HOMOLOGS

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3,4-Benzphenanthrene is the simplest aromatic hydrocarbon possessing a specific carcinogenic activity; the isomeric tetracyclic hydrocarbons, chrysene and 1,2-benzanthracene do not exhibit such activity, although the nucleus of the latter is also present in molecules which are more strongly carcinogenic. Certain homologs of 3,4-benzphenanthrene also possess carcinogenic activity, and this fact has attracted the attention of chemists to hydrocarbons of the benzphenanthrene series and has stimulated the search for methods for their synthesis.

A few methods are known for the preparation of benzphenanthrene homologs. Of the methods related to the Pschorr synthesis the most satisfactory was found to be that proposed by Hewett [1], based on cyclization with the aid of potassium hydroxide into quinolines halogenated in one of the aromatic nuclei of α,β-diarylacrylic acids; investigation of the biological properties of compounds obtained by this route provided fundamental material for the problem of the relation between the carcinogenic properties and the structure of hydrocarbons of this series.

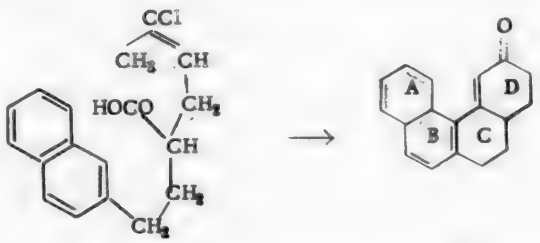
Successful use was also made of some variants of syntheses utilizing intramolecular acylation of γ-aryl butyric acids [2]. Starting materials for these syntheses are compounds of the phenanthrene series in whose molecules is an additional ring. The butyric acid residue necessary for this ring-closure is usually attached to the initial phenanthrene derivative with the help of the classical Reformatsky reaction.

Less suitable methods are those based on the application of the diene synthesis; the yields of adducts in such cases are generally very small. The most promising of the methods of this group is the synthesis based on addition of maleic anhydride to homologs of 1-phenyl-3,4-dihydronaphthalene [3].

It must furthermore be noted that due to the difficult accessibility of the starting substances and the numerous steps in the syntheses, and also due in some cases to the low yields, the hydrocarbons of the 3,4-benzphenanthrene series are even today not readily accessible. The difficulty of preparing compounds of this series has been frequently mentioned in the literature [4].

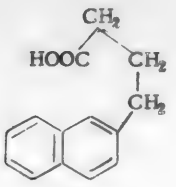
It has been shown [5] that polycyclic ketones and hydrocarbons can be synthesized with the help of sulfuric acid hydrolysis of unsaturated compounds containing a halogen atom at the double bond; on treatment with sulfuric acid, α-(3-chlorocrotyl)-γ-aryl butyric acids undergo hydrolysis and twofold cyclization with formation of polycyclic ketones which can be converted into the corresponding hydrocarbons.

A similar transformation of α-(3-chlorocrotyl)-γ-(2-naphthyl)-butyric acid (I) should lead to ketone (II) containing the 3,4-benzphenanthrene skeleton:



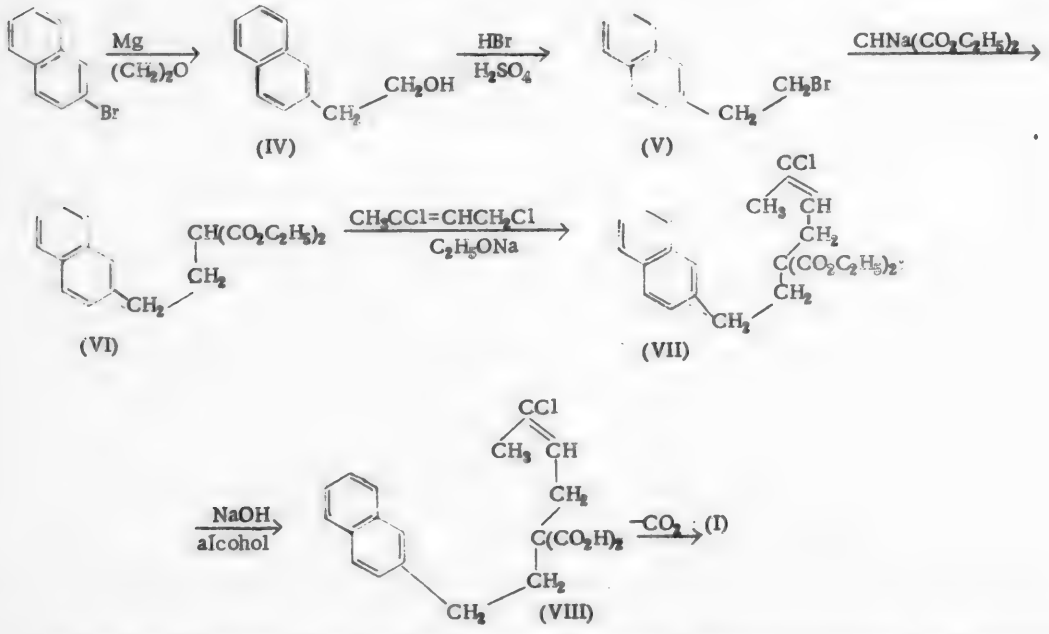
(I) (II)

It would appear that in this case closure of ring C could proceed completely or partially also in another direction with formation of a ketone containing the 1,2-benzanthracene skeleton. However, the literature on the cyclization of γ-(2-naphthyl)-butyric acids not substituted in the side chain suggests that this possibility can be excluded; in all cases when γ-(2-naphthyl)-butyric acid (III) does not contain a substituent in the 8-position, the ring closes at position 1, and the product is a compound of the penanthrene series.



(III)

Use may therefore be made, as starting material for synthesis of compounds of the benzphenanthrene series, of α-(3-chlorocrotyl)-γ-(2-naphthyl)-butyric acid (I), which was obtained according to the scheme below.



The reaction of ethylene oxide with the magnesium derivative of 2-bromonaphthalene was investigated for the first time by Sontage [6] who obtained from 153 g of bromo compound a total of 13 g of impure β-(2-naphthyl)-ethyl alcohol (IV). Karrer and co-workers [7], however, succeeded in obtaining this alcohol by the same route in a yield of 45% of theory. This difference in yields and the poor reproducibility of the experiments were explained by Yu. S. Zalkind [8] who showed that the Grignard reagent from 2-bromonaphthalene is extraordinarily easily oxidized by oxygen of the air, so that the product of the subsequent reaction will always contain a considerable amount of β-naphthol. Using the Grignard solution prepared according to Yu. S Zalkind's instructions in a hydrogen stream, we were able to prepare alcohol (IV) in a yield of 69-70%.

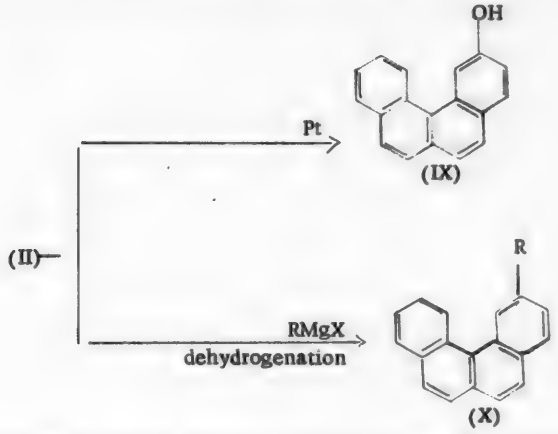
β-(2-Naphthyl)-ethyl bromide (V) was previously prepared by Karrer and coworkers [7] by reacting alcohol (IV) with phosphorous tribromide; they did not state the yield. It was ascertained that bromide (V) may be prepared in 82% yield by boiling a mixture of alcohol (IV) with hydrobromic and sulfuric acids.

Acid (I), as shown in the scheme, was prepared from bromide (V) and 1,3-dichlorobutene-2 by the malonic synthesis. Hydrolysis and double cyclization of acid (I) was effected with the help of sulfuric acid of s.g. 1.78 at 45-55° in a carbon dioxide atmosphere. As was to be expected, the product of cyclization was 6-keto-6,7,8,8a,9,10-hexahydro-3,4-benzphenanthrene (II), which was formed in 69% yield.

Attempts to dehydrogenate this ketone with selenium and sulfur were unsuccessful; with selenium a resin was formed from which it was impossible to isolate a pure substance; with sulfur a crystalline product was obtained which contained sulfur and was not further examined.

On dehydrogenation, however, with platinum black as well as with palladium black, and after removal

of small amounts of neutral products from the dehydrogenated material, there was obtained 6-hydroxy-3,4-benzphenanthrene (IX) in 78% yield. By distillation with zinc dust, this substance was reduced to 3,4-benzphenanthrene which was identified through the picrate. The yield of benzphenanthrene was 50% of the theoretical.



The presence of the carbonyl group provided the possibility of passage from ketone (II) to homologs of benzphenanthrene containing substituents in the 6-position. Since, however, ketone (II) is an α,β-unsaturated ketone another possibility was addition of Grignard reagent at the 1,4-position with formation of saturated ketones substituted at the angular carbon atom 4b. In that case dehydrogenation of the reaction products would be accompanied by cleavage of alkyl groups from the quaternary carbon atom to give 3,4-benzphenanthrene or its 6-hydroxy derivative as end-product. In the present case, however, this course of the reaction would be improbable because addition of an alkyl group to the carbon atom 4b would be sterically hindered.

Dehydrogenation of the product of reaction of ketone (II) with excess of methyl magnesium iodide gave the 6-methyl-3,4-benzphenanthrene previously described by Hewett [1] and it was identified through the picrate. Thus the Grignard reagent had added on at the carbonyl group of the ketone. Similarly, by the action on the ketone of the Grignard reagents prepared from ethyl bromide and bromobenzene there were obtained 6-ethyl- and 6-phenyl-3,4-benzphenanthrenes, not previously described in the literature. These hydrocarbons were obtained in yields of 62-84%.

The 6-methyl homolog, like other monomethyl benzphenanthrenes, is carcinogenically active [9]. In view of the fact that, contrary to expectations, the 9-methyl-10-ethyl-1,2-benzanthracene synthesized by Mikhailov and Chernova [10] did not surpass 9,10-dimethyl benzanthracene in activity [11], it is also of interest to investigate the biological properties of 6-ethyl and 6-phenyl benzphenanthrenes.

EXPERIMENTAL

The initial 2-bromonaphthalene was prepared by the method of Newman and Wise: Thermal decomposition of a mixture of the dry double salt of naphthyl diazonium chloride with mercuric bromide and sodium bromide.

β-(2-Naphthyl)-ethyl alcohol (IV). Into a mixture of 11.4 g active magnesium and a small amount of dry ether was poured a few milliliters of a solution of 100 g 2-bromonaphthalene in 400 ml absolute ether; the mixture was heated to boiling on the water bath and to it was added 2 ml Grignard solution prepared from a mixture of ethyl chloride and 2-bromonaphthalene. After the reaction had started, addition was made to the reaction mixture over a short period of all the remaining 2-bromonaphthalene solution. The reaction was performed at the boil and with continuous passage of a slow stream of dry hydrogen. From time to time the mixture was stirred mechanically. The reaction was substantially completed after 3 hours when 0.5-0.8 g magnesium remained in the flask. The solution was cooled in a freezing mixture and gradual addition was made, with intensive mechanical stirring, of an excess (20-25 g) of ethylene oxide in absolute ether. The thickened mass was left overnight and then boiled on the water bath for 2 hours. The ice-cooled reaction mixture was decomposed with dilute hydrochloric acid and the contents of the flask were then subjected to steam-distillation with the aim of removing unreacted bromonaphthalene and the naphthalene formed by decomposition of the Grignard reagent. Steam-distillation was continued until there was substantially no precipitation of crystalline material on the walls of the condenser. The

organic substance remaining in the flask solidified on cooling and was dissolved in ether; the ether solution was washed with weak alkali and then water before drying with sodium sulfate. The residue after driving off the ether was distilled in vacuum. At 180-184° and 15 mm, 58 g (69.8% of theory) distilled over as a light-yellow liquid which crystallized completely in the receiver. After recrystallization from petroleum ether the colorless crystals melted at 67-68°.

0.1032 g substance: 0.3184 g CO_2; 0.0666 g H_2O. Found %: C 84.14; H 7.17. $C_{12}H_{12}O$. Calculated %: C 83.7; H 6.99.

β-(2-Napnthyl)-ethyl bromide (V). A mixture of 108 g alcohol (IV), 250 ml hydrobromic acid (s.g. 1.52) and 50 ml conc. sulfuric acid was refluxed for 4-5 hours. The mixture was cooled and diluted with water when the bromide crystallized; this was dissolved in ether, washed with alkali and then with water, and dried with sodium sulfate. After driving off the ether the residual crystalline substance was distilled in vacuum when 121.2 g bromide (82% of theory) came over at 138-140° and 3 mm. Colorless crystals with m.p. 64-65°.

0.1123 g substance: 0.0893 g AgBr. 0.1152 g substance: 0.0922 g AgBr. Found %: Br 33.84, 34.05. $C_{12}H_{11}Br$. Calculated %: Br 34 0%

β-(2-Naphthyl)-ethyl malonate (VI). To the sodium ethyl malonate prepared from 14.2 g sodium, 170 g absolute alcohol and 100 g ethyl malonate was added 92 g of crystalline bromide (V). The mixture was boiled for 5 hours. After cooling, the mixture was diluted with water, acidified with hydrochloric acid until weakly acid, the straw-colored liquid product was dissolved in ether, the ether solution washed with water and dried with sodium sulfate. After the solvent had been driven off, the product distilled at 198° and 3 mm. 80 05 g (65.25% of theory) of ester (VI) was obtained.

d_4^{20} 1.0976; n_D^{20} 1.5420.

0.1110 g substance: 0.2260 g CO_2; 0.0732 g H_2O. Found %: C 72 72; H 7.32. $C_{19}H_{22}O_4$. Calculated %: C 72.61; H 7.0.

[β-(2-Naphthyl)-ethyl-(3-chloro)-crotyl]-malonate (VII). To a solution of sodium alcoholate prepared from 4.4 g sodium and 50 ml absolute alcohol was added 59 g of the monosubstituted malonate (VI). The mixture was heated on the water bath for 30 min., after which it was cooled to room temperature. Gradual addition was then made of 30 g freshly distilled 1,3-dichlorobutene-2. The mixture was refluxed for 5 hours, then cooled, and addition made of dilute hydrochloric acid in amount sufficient to dissolve the formed salt. The product was extracted with ether, the ether solution washed with water and dried with sodium sulfate. After driving off the ether, the product distilled at 230-231° at 3mm, giving 61.9 g (81.8% of theory) of the disubstituted malonate (VII) as a viscous, light-yellow liquid.

d_4^{20} 1.123; n_D^{20} 1.5460.

0.1134 g substance: 0.0413 g AgCl. 0.1132 g substance: 0.0414 g AgCl. Found %: Cl 9.01, 9.05. $C_{23}H_{27}O_4Cl$. Calculated %: Cl 8.81

[β-(2-Naphthyl)-ethyl-(3-chloro)crotyl]-malonic acid (VIII). A mixture of 90 g ester (VII), 27.2 g sodium hydroxide and 380 g 90% alcohol was boiled on the water bath for 4 hours, following which 150 ml water was added and the alcohol completely distilled off. The solution was acidified with hydrochloric acid when a heavy oil separated. The substance was dissolved in ether, washed with water and dried with sodium sulfate. The crystalline substance remaining after removal of the ether was washed with benzene There was obtained 56 g (70% of theory) of colorless, thin crystals with m.p. 167°

0.1128 g substance: 0.0490 g AgCl. 0.1072 g substance: 0.0458 g AgCl. Found %: Cl 10.75, 10.57. $C_{19}H_{19}O_4Cl$. Calculated %: Cl 10.25.

α-(3-Chlorocrotyl)-γ-(2-naphthyl)-butyric acid (I). 10 g of the pure dibasic acid (VII) was decomposed by heating over the naked flame. The resultant thick oil was distilled at 234-235° at 4 mm, giving 8.3 g (95% of theory) of a light-yellow, viscous oil.

d_4^{20} 1.1568; n_D^{20} 1.5848.

0.1143 g substance: 0.0510 g AgCl. 0.1291 g substance: 0.0630 g AgCl. Found %: Cl 12.10, 12.08. $C_{18}H_{19}O_2Cl$. Calculated %: Cl 11.73.

6-Keto-6,7,8,8a,9,10-hexahydro-3,4-benzphenanthrene (II). To 70 g of 84.5% sulfuric acid was added 7 g acid (I). After standing for a short period at room temperature, the mixture was heated on the water bath at 45-55° in a stream of carbon dioxide for 30 min. The heating was attended with copious evolution of hydrochloric acid. After the substance had completely gone into solution and the evolution of hydrochloric acid had ceased, the dark-red solution was left overnight at room temperature. On the following day the contents of the flask were poured on to ice, the resultant grey precipitate was filtered, carefully washed with dilute alkali and then with water, dried, and recrystallized from alcohol. There was obtained 4 g (69.68% of theory) of colorless crystals with m.p. 125-126°.

0.1203 g substance: 0.3830 g CO_2; 0.0733 g H_2O. 0.1120 g substance: 0.357 g CO_2; 0.0672 g H_2O. Found %: C 86.82, 86.93; H 6.07, 6.66. $C_{18}H_{16}O$. Calculated %: C 87.09; H 6.45.

The 2,4-dinitrophenylhydrazone was prepared in an alcoholic medium and recrystallized from chloroform. Red crystals, m.p. 173-174°.

0.1005 g substance: 12 ml N_2 (22°, 683 mm). 0.0715 g substance: 8.8 ml N_2 (27°, 680 mm). Found %: N 12.43, 12.52. $C_{24}H_{20}N_4O_4$. Calculated %: N 13.00.

Dehydrogenation of ketone (II) with sulfur. A mixture of 1 g ketone (II) and 0.3 g powdered sulfur was heated at 210° for 30 minutes until no more hydrogen sulfide came off, and the contents of the flask were transferred to a porcelain beaker and thoroughly triturated with dilute alkali, then filtered and washed with water. The substance retained on the filter was dissolved in alcohol; the alcoholic solution was digested with active carbon, filtered, and diluted with water. The resultant light-yellow acicular crystals melted at 172-173°. The product contained sulfur.

0.1024 g substance: 0.056 g $BaSO_4$. 0.1109 g substance: 0.059 g $BaSO_4$. Found %: S 7.56, 7.30.

6-Hydroxy-3,4-benzphenanthrene (IX). A mixture of 0.8 g catalyst (palladium on carbon, 5% metal content) and 2 g ketone (II) was heated in a carbon dioxide stream at 300-320° for 1 hour. The product was extracted with benzene, the solution filtered off, treated with dilute alkali solution and dried. After removal of the benzene there was not a large amount of neutral dehydrogenation products. Acidification of the alkaline solution led to separation of a viscous oil which was dissolved in ether. After removal of the ether, the residue was dissolved in alcohol and the alcoholic solution digested with active carbon. Dilution of the filtered solution with water brought down white, fluffy crystals in an amount of 1.55 g (78.8% of theory). M.p. of the colorless crystals 108-110°.

0.1034 g substance: 0.3350 g CO_2; 0.049 g H_2O. Found %: C 88.35; H 5.26. $C_{18}H_{12}O$. Calculated %: C 88.52; H 4.91.

The dark-red picrate, recrystallized from alcohol, had m.p. 147-148°.

0.0728 g substance: 6.2 ml N_2 (21°, 680 mm). Found %: N 8.85. $C_{24}H_{15}N_3O_8$. Calculated %: N 8.88.

3,4-Benzphenanthrene. A homogeneous mixture of 1.5 g 6-hydroxy-3,4-benzphenanthrene and 12 g zinc dust was heated in a quartz test tube to dark-red heat and the heating continued until no more viscous, dark oil separated. The product was dissolved in ether, the solution was washed with alkali and then with water and dried with sodium sulfate. The oil remaining after removal of the ether was rubbed with a small amount of alcohol, when it crystallized. The alcoholic solution of the substance was digested with active carbon, and the greater part of the solvent was driven off from the filtered solution. A precipitate of colorless acicular crystals was formed in quantity of 0.7 g (50% of theory, m.p. 67-68°.

0.1023 g substance: 0.3557 g CO_2; 0.0536 g H_2O. Found %: C 94.82; H 5.82. $C_{18}H_{12}$. Calculated %: C 94.73; H 5.27.

The picrate had a brick-red color and melted at 126° (from alcohol).

0.0986 g substance: 9.1 ml N_2 (23°, 677 mm). 0.0940 g substance: 8.6 ml N_2 (23°, 677 mm). Found %: N 9.33, 9.47. $C_{24}H_{15}N_3O_7$. Calculated %: N 9.20.

6-Methyl-, 6-ethyl- and 6-phenyl-3,4-benzphenanthrenes (X). These hydrocarbons were prepared in the following manner: To a Grignard reagent prepared from a 3- to 4-fold molar excess of the corresponding alkyl (aryl) halide was added 6-10 g ketone (II); the mixture was boiled on the water bath for 2 hours and left overnight.

While cooling with ice-water, the reaction mixture was decomposed by addition of water and dilute hydrochloric acid, the product was extracted with ether, and the ethereal solution was washed and dried. Removal of the ether left a viscous oil which was dehydrogenated with platinum black (approximately 0.1 g black per 1 g substance) at 300-320° for about 30 min. The product was extracted with benzene, the benzene solution was filtered from catalyst, and the benzene removed. Phenyl benzphenanthrene was obtained in the crystalline form after removal of the benzene. The methyl and ethyl benzphenanthrenes were distilled in vacuum. The ethyl derivative crystallized in the receiver during the distillation, but the methyl compound was only obtained in the crystalline form after conversion of the vitreous product into the picrate, recrystallization of the picrate from methyl alcohol and decomposition with aqueous ammonia. The hydrocarbons, likewise the picrates, were purified by recrystallization from ethyl alcohol, with the exception of the picrate of phenyl benzphenanthrene which was purified with the help of benzene since it decomposed into its constituents when treated with alcohol.

In the table are shown the properties and yields of the hydrocarbons and their picrates, also the analytical data.

R-	B.p.	M.p.	Yield (in % of theory)	Analysis				M.p. of picrate	Analysis of picrate	
				Found %		Calculated %			Found %	Calcd. %
				C	H	C	H		N	N
CH_3	206-208° (2 mm)	80-81°	76.92	94.06	5.94	94.21	5.78	–	–	–
C_2H_5	215-218 (2.5 mm)	82-83	62	93.88	6.54	94.75	6.25	104-105°	8.93	8.66
C_6H_5	–	127-128	84.35	94.77	5.72	94.73	5.47	107-108	8.17	7.88

SUMMARY

It is shown that under the action of sulfuric acid, α-(3-chlorocrotyl)-γ-(2-naphthyl)butyric acid undergoes hydrolysis and double cyclization to form 6-keto-6,7,8,8a,9,10-hexahydro-3,4-benzphenanthrene. Dehydrogenation of this ketone gave 3,4-benzphenanthrene in 50% yield.

The above α,β-unsaturated ketone adds on alkyl magnesium halides at the double bond of the carbonyl group. 6-Methyl-, 6-ethyl- and 6-phenyl-3,4-benzphenanthrenes were synthesized by dehydrogenation of the products of reaction of the ketone with the corresponding Grignard reagents.

LITERATURE CITED

[1] C. L. Hewett, J. Chem. Soc. 1286 (1938); 293 (1940); J. L. Everett, C. L. Hewett, J. Chem. Soc., 1159 (1940).

[2] W. E. Bachmann. R. O. Edgerton, J. Am. Chem. Soc. 62, 2970 (1940); M. S. Newmann, W. B. Wheatley, J. Am. Chem. Soc. 70, 1913 (1948).

[3] J. Szwuszkowicz, J. Modest, J. Am. Chem. Soc. 70, 2542 (1948); 72, 566 (1950).

[4] C. L. Hewett, J. Chem. Soc., 596 (1936); J. Cook, M. Robinson, J. Chem. Soc. 505, (1938).

[5] G. T. Tatevosyan and A. G. Vardanyan, J. Gen. Chem. 17, 1528 (1947); G.T.Tatevosyan and S.A. Vardanyan, J. Gen. Chem., 19, 332 (1949); see Consultants Bureau translation, p. 293.

[6] D. Sontag, Ann. Chim. (11) 1, 359 (1934).

[7] P. Karrer, A. Geiger, A. Ruegger, C. Schwab, Helv. Chim. Acta. 23, 585 (1940).

[8] Yu. S. Zalkind, J. Gen. Chem. 4, 807 (1934).

[9] G. M. Badger, J. W. Cook, C. L. Hewett, E. L. Kennaway, N. M. Kennaway, R. H. Martin, A. M. Robinson, Pr.Roy. Soc. (London), B 129, 439 (1940).

[10] B. M. Mikhailov and N. G. Chernova, Proc. Acad. Sci. USSR, 20, 585 (1938).

[11] B. M. Mikhailov and A. N. Blokhina, J. Gen. Chem. 10, 1793 (1940).

[12] M. S. Newmann, P. Wise, J. Am. Chem. Soc. 63, 2847 (1941).

Received January 12, 1951

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ALKANE SULFONIC ACIDS

IV. REACTIONS OF ALKANESULFOCHLORIDES WITH BENZIDINE

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The objective of this investigation was the study of the reaction of alkane sulfochlorides with a more complex amine, namely, the bicyclic-diamine benzidine [1]. This reaction could proceed according to one of the schemes below or according to the two schemes concurrently:

1. $RSO_2Cl + NH_2C_6H_4{\cdot}C_6H_4NH_2 = RSO_2NHC_6H_4{\cdot}C_6H_4NH_2 + HCl$;
2. $2RSO_2Cl + NH_2C_6H_4{\cdot}C_6H_4NH_2 = RSO_2NHC_6H_4{\cdot}C_6H_4NHSO_2R + 2HCl$,

i.e. in the first case a mono-(alkanesulfo)-benzidide could be formed and in the other a di-(alkanesulfo)-benzidide.

We proceeded to investigate this reaction, also the effect of the conditions, particularly solvents and temperatures. The reaction was performed by heating to 70° and also at room temperature, using alcohol or pyridine as reaction media. Examination of the reaction products revealed that in all cases di-(alkanesulfo)-benzidide is formed, and, as a rule, benzidine hydrochloride is obtained as a secondary product. Thus the reaction proceeds according to the scheme:

$$2RSO_2Cl + 2NH_2C_6H_4{\cdot}C_6H_4NH_2 = RSO_2NHC_6H_4{\cdot}C_6H_4NHSO_2R + HCl{\cdot}NH_2C_6H_4{\cdot}C_6H_4NH_2{\cdot}HCl.$$

We reacted methane-, ethane- and butanesulfochlorides with benzidine. The reaction products were grey-pink, amorphous powders, melting above 200° with decomposition, very difficultly soluble in the majority of solvents. In the cold they dissolve fairly readily in pyridine, and when heated they partially dissolve in alcohol. They dissolve in alkali from which they are brought down by acidification with dilute sulfuric or hydrochloric acid. This property was exploited in separating them from by-products.

EXPERIMENTAL

1. Reaction of methanesulfochloride with benzidine in a pyridine medium. To 2.4 g benzidine dissolved in 10 ml pyridine was gradually added 1.5 g methanesulfochloride. The temperature rose to 70-75° and a dark-red precipitate came down. The reaction mixture was left for 24 hours at room temperature, and the precipitate then collected and dried. Examination of the solubility of the precipitate in water revealed that a portion was readily soluble and went into solution, while a portion remains undissolved, thus demonstrating the heterogeneity of the crude product. Two methods were used for separating the components.

a) Half of the crude product was treated with boiling water, a portion going into solution. A grey-white crystalline substance came down from the solution on cooling, and was identified, through the nitrogen determination, as benzidine hydrochloride.

0.1057 g substance: 8.12 ml 0.1 N H_2SO_4. Found %: N 10.74. $C_{12}H_{14}N_2Cl_2$. Calculated %: N 10.89.

The water-insoluble portion was found to contain nitrogen and sulfur but no halogen. The analytical data are consistent with it being the basic reaction product, di-(methanesulfo)-benzidide with the structure $CH_3SO_2NHC_6H_4{-}C_6H_4NHSO_2CH_3$.

0.1240 g substance: 7.13 ml 0.1 N. H_2SO_4. Found %: N 8.05. $C_{14}H_{16}O_4N_2S_2$. Calculated %: N 8.23.

The product was purified by dissolving in pyridine and precipitating with water. It melts above 200° with decomposition.

b) Our second method of separating the reaction product from benzidine hydrochloride was based on the solubility in alkali and on the separation of the product when the alkaline solution was acidified. The second half of the crude product was dissolved in 5% alkali; the undissolved residue was filtered off and the alkaline filtrate acidified with 5% sulfuric acid until the turbidity did not disappear. After standing for a short

period with cooling, a pinkish amorphous product came down and was filtered, washed with water and dried. In its properties it resembled the product isolated in the aqueous treatment, as was confirmed by analysis. The over-all yield of the product isolated by both methods was 50% of the theoretical. The same product is formed by heating on a water bath under a reflux condenser for one hour, i.e. di-(methanesulfo)-benzidide.

2. Reaction of methanesulfochloride with benzidine in alcohol. 2.7 g benzidine was dissolved in 30 ml absolute alcohol by heating on the water bath. To the solution, cooled to room temperature, was added 1.6 g methane sulfochloride in small portions. A light-pink precipitate came down and, after collection, was separated into its components by the above-described method. The total yield of di-(methanesulfo)-benzidide was 59%. The same product is obtained in 70% yield by refluxing on the water bath under the same conditions in an alcoholic medium. Consequently, in all the conditions employed by us, one and the same products are formed: di-(methanesulfo)-benzidide and (as by-product) benzidine hydrochloride.

3. Reaction of ethanesulfochloride with benzidine in pyridine. 3 g benzidine, 12 ml pyridine and 2.1 g ethanesulfochloride were taken. The reaction course and the separation of products were conducted as above. The properties of the isolated di-(ethanesulfo)-benzidide resembled those of di-(methanesulfo)-benzidide. It melts above 200° with decomposition. It was recrystallized from pyridine and water. Yield 50% of theory. Reaction in pyridine with heating gives a 58% yield of di-(ethanesulfo)-benzidide.

0.1500 g substance; 7.99 ml 0.1 N H_2SO_4. Found %: N 7.45. $C_{16}H_{20}O_4N_2S_2$. Calculated %: N 7.60.

4. Reaction of ethanesulfochloride with benzidine in alcohol. 4.6 g benzidine was mixed with 40 ml absolute alcohol and 3.2 g ethanesulfochloride. Further procedure was as above. Yield 72% of the theoretical. Reaction in alcohol with heating gave 78% yield. Regardless, therefore, of our experimental conditions, ethanesulfochloride gives di-(ethanesulfo)-benzidide as the main product and benzidine hydrochloride as by-product.

5. Reaction of butane sulfochloride with benzidine in alcohol. 2.9 g benzidine, 25 ml absolute alcohol and 2.5 g butanesulfochloride were taken. Further treatment was as above. Yield of di-(butanesulfo)-benzidide 60%; its crystalline structure was more strongly defined and it was more easily soluble in alcohol than the above-described methane- and ethanesulfobenzidides. It likewise melts above 200° with decomposition.

0.0892 g substance: 3.85 ml 0.1 N H_2SO_4. Found %: N 6.04. $C_{20}H_{28}O_4N_2S_2$. Calculated %: N 6.60.

SUMMARY

1. Di-(methanesulfo)-, di-(ethanesulfo)- and di-(butanesulfo)-benzidides have been prepared and characterized.

2. It is shown that the reaction proceeds in one direction regardless of the conditions, namely, with formation of di-(alkanesulfo)-benzidide and benzidine hydrochloride.

3. The reaction is shown to proceed more completely in an alcoholic medium when heated.

LITERATURE CITED

[1] A. G. Kostsova, J. Gen. Chem., 11, 63 (1941); J. Gen. Chem. 18, 729 (1948); J. Gen. Chem. 19, 346 (1949); see Consultants Bureau translation, p. 307.

Received April 17, 1950

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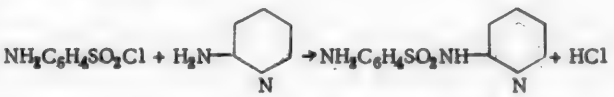
ALKANESULFONIC ACIDS

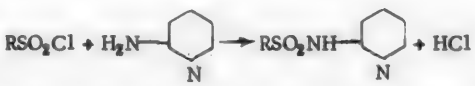
V. REACTION OF ALKANESULFOCHLORIDES WITH α-AMINOPYRIDINE AND SULFANILAMIDE

A. G. Kostsova

The purpose of the investigation was the study of the reaction of alkanesulfochlorides with α-aminopyridine and sulfanilamide. One of the most important derivatives of α-aminopyridine in the aromatic series is sulfidine, in which the sulfanilic acid residue is linked to the α-aminopyridine residue. The reaction is represented by the following equation:

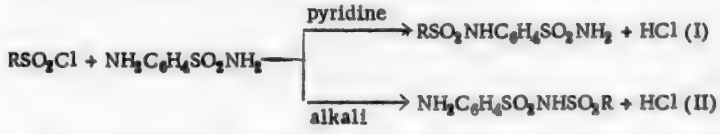


We wished to perform the reaction with alkanesulfochlorides according to the above scheme:



We see from the above equations that the product which we had in view must be similar in structure to sulfidine, but differs from the latter in containing an aliphatic radical in place of the $NH_2C_6H_4$ group characteristic of sulfidine. Since our investigations are largely concerned with the interaction of alkanesulfochlorides with aromatic amines [1], it was of interest also to study the reaction with α-aminopyridine with methane-, ethane-, 2-methylethane-, butane-, 2-methylpropane- and 2-methylbutanesulfochlorides. Experiments showed that the reactions proceed best of all in benzene at room temperature. The products are alkane sulfo-α-aminopyridides (main products) and a yellow, heavy oil which appears to be a mixture of unreacted α-aminppyridine and its hydrochloride. 2-Methylethane-sulfochloride is somewhat exceptional in that it forms, under these conditions, a negligible amount of 2-methylethane sulfo-α-aminopyridide, whereas when the reaction is performed in acetone with heating the results are entirely satisfactory. The reaction product — 2-methylethane sulfo-α-aminopyridide — also differs from the derivatives of the other sulfochlorides in being readily soluble in water in the cold, whereas all the others only dissolve in water when boiled and come down again on cooling. Its melting point is much higher in comparison with the other members of the series. These differences are evidently the consequence of structural features of 2-methylethylsulfo-α-aminopyridide in which the sulfamidine group is attached to the secondary carbon whereas in the other compounds it is at a primary carbon.

The reaction of alkanesulfochlorides with sulfanilamide has been described in the literature [2,3]. The reaction was performed in pyridine and in an alkaline medium. It was shown that its course varies with the medium. Thus in pyridine, N^4-alkanesulfosulfanilamide is formed, and in alkali N^1-alkanesulfosulfanilamide, which may be represented by the following scheme:



We conducted the reaction between alkanesulfochlorides and sulfanilamide in an acetone medium with heating on the water bath under a reflux condenser. The constants and the properties of the compounds which we prepared show that under our experimental conditions N^4-alkanesulfosulfanilamides are formed, i.e. the reaction proceeds according to variant (I) in the above scheme.

Sulfanilamide was reacted with methane-, ethane- and 2-methylpropanesulfochlorides. The table lists the compounds prepared, their melting points and their solubilities.

Compounds	Formulas	M.p.	Solubility				
			Water	Alcohol	Alkali	Acetone	Benzene
Methanesulfo-α-aminopyridide	$CH_3SO_2NHC_5H_4N$	194°	Poor	Poor	Good	Good	Good
Ethanesulfo-α-aminopyridide	$CH_3CH_2SO_2NHC_5H_4N$	163					
2-Methylethanesulfo-α-aminopyridide	$(CH_3)_2CHSO_2NHC_5H_4N$	203	Good	Poor	Good	Poor	Poor
Butanesulfo-α-aminopyridide	$CH_3CH_2CH_2CH_2SO_2NHC_5H_4N$	97	Poor	Poor	Good	Good	Good
2-Methylpropanesulfo-α-aminopyridide	$(CH_3)_2CHCH_2SO_2NHC_5H_4N$	103					
2-Methylbutanesulfo-α-aminopyridide	$(CH_3)_2CHCH_2CH_2SO_2NHC_5H_4N$	108					
N^4-Methanesulfoanilamide	$CH_3SO_2NHC_6H_4SO_2NH_2$	181	Poor	Good	Good	Good	Good
N^4-Ethanesulfosulfanilamide	$CH_3CH_2SO_2NHC_6H_4SO_2NH_2$	176					
N^4-2-Methylpropanesulfosulfanilamide	$(CH_3)_2CHCH_2SO_2NHC_6H_4SO_2NH_2$	151					

EXPERIMENTAL

1. Preparation of methanesulfo-α-aminopyridide. 4.9 g α-aminopyridine (recrystallized from petroleum ether) and 3 g methanesulfochloride were dissolved in 40 ml benzene. A little heat was developed during mixing. A reddish-brown oil settled to the bottom of the flask together with fine crystals. The benzene was evaporated. The mixture of oil and crystals was treated with cold alcohol which dissolved the oil but not the crystals. The latter were filtered off and the oil solution distilled. The alcohol was driven off on the water bath and the residue distilled in vacuum (b.p. 106° at 20 mm). Only a negligible amount came over under these conditions and rapidly crystallized. The greater part of the oil decomposed. The crystalline product melted at 55°. A nitrogen determination showed this to be unreacted α-aminopyridine. The part of the oil which decomposed during distillation was apparently a mixture of α-aminopyridine hydrochloride and α-aminopyridine. The fine crystals were dried and recrystallized from water (or acetone). Yield 35% of the theoretical.

0.0422 g substance: 4.85 ml 0.1 N H_2SO_4. Found %: N 16.16. $C_6H_8O_2N_2S$. Calculated %: N 16.27.

2. Preparation of ethanesulfo-α-aminopyridide. 2.9 g α-aminopyridine and 2 g ethanesulfochloride were dissolved in 40 ml benzene. In this case a crystalline product was not precipitated at once. The benzene solution, separated from the oil, was evaporated in a porcelain beaker; with progressive evaporation of the benzene the sides of the beaker became more and more covered with white crystals of ethanesulfo-α-aminopyridide. It was recrystallized from water. Yield 45% of the theoretical.

0.1035 g substance: 11.3 ml 0.1 N H_2SO_4. Found %: N 15.28. $C_7H_{10}O_2N_2S$. Calculated %: N 15.05.

3. Preparation of 2-methylethanesulfo-α-aminopyridide.* In this case the acetone was used as reaction medium because in benzene the yields are negligible. 2.4 g α-aminopyridine was dissolved in 15 ml anhydrous acetone and dropwise addition was made of 2 g 2-methylethanesulfochloride. Slight heat was developed. The reaction was completed by heating on the water bath. A layer of viscous yellow oil was formed and fine white crystals settled out at the same time. The acetone was distilled off and the oil drained from the crystals on a Schott filter. The crystals were recrystallized from alcohol since in water, in contrast to the previous material, they were readily soluble in the cold. Yield 40% of theory. Reactions conducted in acetone with cooling (+2°) and at room temperature gave yields of 35-37%.

0.1181 g substance: 11.73 ml 0.1 N H_2SO_4. 0.0950 g substance: 0.1083 g $BaSO_4$. Found %: N 13.90; S 15.63. $C_8H_{12}O_2N_2S$. Calculated %: N 13.99; S 16.02.

4. Preparation of butanesulfo-α-aminopyridide. 2.8 g α-aminopyridine and 2.3 g butanesulfochloride were dissolved in 30 ml benzene. Further treatment was as for the preparation of methane- and ethanesulfo-α-aminopyridides. The crystals were separated from the oil, washed with alcohol, and recrystallized from water.

*Compound prepared and characterized by O.I.Strepetova.

Needles. Yield 32% of theory.

0.0924 g substance: 8.19 ml 0.1 N H_2SO_4. Found %: N 12.40. $C_9H_{14}O_2N_2S$. Calculated %: N 13.08.

5. Preparation of 2-methylpropanesulfo-α-aminopyridide. 2.4 g α-aminopyridine and 2 g 2-methylpropanesulfochloride were dissolved in 40 ml benzene. The crystals remaining after evaporation of the benzene were well-formed prisms. Recrystallized from water. Yield 30% of theory.

0.0812 g substance: 7.38 ml 0.1 N H_2SO_4. Found %: N 12.72. $C_9H_{14}O_2N_2S$. Calculated %: N 13.08.

6. Preparation of 2-methylbutanesulfo-α-aminopyridide.* 2.2 g α-aminopyridine and 2 g 2-methylbutanesulfochloride were dissolved in 40 ml benzene. The reaction products were isolated as before. Yield 48% of theoretical. When the reaction in benzene was carried out with application of heat, the yield fell to 11% and the amount of oil sharply increased. Reaction in ice resulted in a yield of about 34%.

0.1142 g substance: 10 ml 0.1 N H_2SO_4. 0.1720 g substance: 0.1780 g $BaSO_4$. Found %: N 12.26; S 14.19. $C_{10}H_{16}O_2N_2S$. Calculated %: N 12.28; S 14.03.

The oil isolated in all these reactions behaves similarly, i.e. on distillation a small amount of α-aminopyridine comes over while the main bulk decomposes. Its composition has consequently not been finally established.

The prepared alkanesulfo-α-aminopyridides are fairly stable to hydrolysis. Thus, for example, when they are boiled in water, alkali and acid and then cooled, they are quantitatively recovered unchanged. In the case of the alkaline solution, the products only come down after acidification with a strictly equivalent amount of acid. If an excess of acid is used, the product again goes into solution because a salt is apparently formed at the expense of the hetero atom of the pyridine ring.

7. Preparation of N^4-methanesulfosulfanilamide. A mixture of 4 g sulfanilamide, 1.7 g methanesulfochloride and 25 ml acetone was refluxed on the water bath for 3 hours. At the end of the reaction the precipitated sulfanilamide hydrochloride was separated and the acetone solution was evaporated. The residue was recrystallized from aqueous alcohol. Yield 83% of the theoretical.

0.060 g substance: 4.73 ml 0.1 N H_2SO_4. Found %: N 11.03. $C_7H_{10}O_4N_2S_2$. Calculated %: N 11.20.

8. Preparation of N^4-ethanesulfosulfanilamide. 2 g ethanesulfochloride and 5 g sulfanilamide were taken in 25 ml acetone. Further procedure as above. Yield 52% of the theoretical.

0.1638 g substance: 12.61 ml 0.1 N H_2SO_4. Found %: N 10.77. $C_8H_{12}O_4N_2S_2$. Calculated %: N 10.60.

9. Preparation of N^4-2-methylpropanesulfosulfanilamide. 2 g 2-methylpropanesulfochloride and 2.3 g sulfanilamide were reacted in 20 ml acetone. Separation and purification of product were carried out as above.

0.0930 g substance: 6.35 ml 0.1 N H_2SO_4. Found %: N 9.55. $C_{10}H_{16}O_4N_2S_2$. Calculated %: N 9.58.

SUMMARY

1. Methane-, ethane-, 2-methylethane-, 2-methylpropane-, butane- and 2-methylbutanesulfo-α-aminopyridides have been prepared for the first time and characterized.

2. The exceptional behavior of 2-methylethanesulfochloride in its reaction with α-aminopyridine is shown in relation to solvents and in relation to the properties of the resultant 2-methylethanesulfo-α-aminopyridide.

3. N^4-Methane, N^4-ethane- and N^4-2-methylpropanesulfosulfanilamides have been prepared and characterized.

LITERATURE CITED

[1] A. G. Kostsova, J. Gen. Chem., 11, 63 (1941); J. Gen. Chem. 18, 729 (1948); J. Gen. Chem.19, 346(1949).**

[2] Northey, Crossley and co-workers, J. Am. Chem. Soc. 62, 1415 (1940).

[3] J. Sprague, Burney and co-workers, J. Am. Chem. Soc. 62, 1714 (1940).

Received April 17, 1950

Voronezh State University

* Compound prepared and characterized by V. I. Sergeeva.

** See Consultants Bureau translation, p. 307.

ALKANESULFONIC ACIDS

VI. REACTIONS OF ALKANESULFOCHLORIDES WITH ANILINE AND p-ANISIDINE

A. G. Kostsova

As we have already pointed out in previous communications [1], N-substituted amides of alkanesulfonic acids have only recently been the subject of investigation. Some of them were prepared in our laboratory. These include acyl amides, anilides, p-toluidides, phenetidides, α- and β-naphthylamino derivatives of chloromethane- and α-chloroethanesulfonic acids.

Among other Russian researches in this field reference may be made to the work of Melnikov [2] which occupies a rather special place in the sense that we have in view chiefly N-alkyl- and aryl-substituted amides, whereas this author prepared a whole series of N-dichloramides of alkanesulfonic acids possessing high germicidal activity. Incidentally we may say that all the N-dichloramides of chloromethanesulfonic acids described by Melnikov were prepared by us (as that author also notes) as far back as 1935 [3].

Interest in the alkanesulfonic acids and their derivatives grows each year since the sulfonic acids and their diverse derivatives (acid chlorides, amides, N-substituted amides, esters, etc.) have found practical application in various branches of the chemical industry [4]. Our present investigation concerns N-aryl amides of unsubstituted alkanesulfonic acids. Of these the p-toluidides and the p-phenetidides have been fairly closely described in the literature [5]. We considered it of interest to perform the reaction of alkanesulfochlorides with aniline and p-anisidine. The reaction of alkanesulfochlorides with aniline has been inadequately studied. There are short notes in the literature on the anilide of methanesulfonic acid and certain other anilides [6]. We have prepared and described the anilides of chloromethane- and α-chloroethanesulfonic acids [1]. In the present investigation we have prepared the anilides of methane-, ethane-, 2-methylethane-, 2-methylpropane- and 2-methylbutanesulfonic acids. The reaction was carried out in ether as the medium, using one equivalent of sulfochloride to two equivalents of aniline in accordance with the equation:

$$RSO_2Cl + 2C_6H_5NH_2 = RSO_2NHC_6H_5 + C_6H_5NH_2 \cdot HCl.$$

The prepared amides present a twofold interest: 1) They are interesting for the problem of the effect of substituents in the benzene ring upon the properties of the compounds; 2) the reaction of anilide formation can be applied to separation of primary and secondary amines as has been done with aromatic sulfochlorides [7]. Separation is based on the ability of primary amines to form products with sulfochlorides which are soluble in alkalis, while secondary amines give products which are insoluble in alkalis.

We are the first to have carried out the reactions of alkanesulfochlorides with p-anisidine. The reactions proceed according to the above scheme. They were carried out under the same conditions as for aniline. We have prepared ethane- and 2-methylethanephenetidides. The first of these is mentioned in the literature [5]. Latimer and Bost obtained it by reacting ethanesulfochloride with p-phenetidine in a pyridine medium. We repeated the preparation in an ethereal medium. The second was prepared by us for the first time. We prepared the anilides and p-anisidides of methane-, ethane-, 2-methylethane-, 2-methylpropane-, 2-methylbutanesulfonic acids and the p-phenetidides of ethane- and 2-methylethanesulfonic acids, whose properties are set out in Tables 1 and 2.

We see from these tables that all the compounds are crystalline and have well-defined melting points which can be used for identification of alkanesulfonic acids. It is noteworthy that the melting points of derivatives of 2-methylethanesulfonic acid are much higher than those of neighboring members of the series. Evidently the effect of the location of the sulfamide group at the secondary carbon is here manifested. These tables also show that the introduction of alkoxyl groups (CH_3O, C_2H_5O) into the aromatic nucleus of anilides usually raises the melting point. The good solubility of these compounds in alkalis was utilized for their separation from the reaction mixture; they were subsequently precipitated by acid from the alkaline solution. We recrystallized the

reaction products from hot water or by dissolving them in a little alcohol and precipitating with water.

TABLE 1

Anilides of alkanesulfonic acids

Name of compounds	Formula	M.p.	Solubility				
			Water	Alkali	Benzene	Ether	Alcohol
Methanesulfanilide	$CH_3SO_2NHC_6H_5$	96*	Poor	Good	Good	Good	Good
Ethanesulfanilide	$CH_3CH_2SO_2NHC_6H_5$	55					
2-Methylethanesulfanilide	$(CH_3)_2CHSO_2NHC_6H_5$	84					
2-Methylpropanesulfanilide	$(CH_3)_2CHCH_2SO_2NHC_6H_5$	37					
2-Methylbutanesulfanilide	$(CH_3)_2CHCH_2CH_2SO_2NHC_6H_5$	42					

TABLE 2

p-Anisidides and p-phenetidides of alkanesulfonic acids

Name of compounds	Formula	M.p.	Solubility				
			Water	Alkali	Benzene	Ether	Alcohol
Methanesulfanisidide	$CH_3SO_2NHC_6H_4OCH_3$	114*	Poor	Good	Good	Good	Good
Ethanesulfanisidide	$CH_3CH_2SO_2NHC_6H_4OCH_3$	63					
2-Methylethanesulfanisidide	$(CH_3)_2CHSO_2NHC_6H_4OCH_3$	78					
2-Methylpropanesulfanisidide	$(CH_3)_2CHCH_2SO_2NHC_6H_4OCH_3$	45					
2-Methylbutanesulfanisidide	$(CH_3)_2CHCH_2SO_2NHC_6H_4OCH_3$	56					
Ethanesulfophenetidide	$CH_3CH_2SO_2NHC_6H_4OC_2H_5$	80					
2-Methylethanesulfophenetidide	$(CH_3)_2CHSO_2NHC_6H_4OC_2H_5$	95					

EXPERIMENTAL*

The starting sulfochlorides were prepared as described in preceding communications [1].** The aniline and the p-phenetidine were freshly distilled; the p-anisidine was recrystallized from water.

1. Preparation of methanesulfanilide. 2 g methanesulfochloride, 3.2 g aniline and 30 ml absolute ether were refluxed on the water bath. At the end of the reaction the precipitated aniline salt was separated; the ethereal filtrate was either evaporated or the ether was distilled off. The residue was dissolved in dilute alkali (5%) and precipitated with dilute sulfuric acid. Yield 40% of the theoretical.

0.0650 g substance. 3.8 ml 0.1 N H_2SO_4. 0.0989 g substance: 0.1365 g $BaSO_4$. Found %: N 8.18; S 18.92. $C_7H_9O_2NS$. Calculated %: N 8.18; S 18.71.

2. Preparation of ethanesulfanilide. 4.35 g ethanesulfochloride and 6.3 g aniline were reacted in 40 ml ether. The product was separated and purified as above. Yield 65% of the theoretical.

0.0800 g substance: 4.24 ml 0.1 N H_2SO_4. 0.090 g substance: 0.1134 g $BaSO_4$. Found %: N 7.42; S 17.28. $C_8H_{11}O_2NS$. Calculated %: N 7.56; S 17.29.

3. Preparation of 2-methylethanesulfanilide. 2 g 2-methylethanesulfochloride and 2.6 g aniline were reacted in 25 ml ether. Further procedure as above. Yield 53% of the theoretical. Reaction in ether at room temperature gives the same product in 50% yield. Reaction in benzene with heating gives a yield of 57%, without heating a yield of 43%. Reaction without a solvent gives a yield of 64-65%. In the latter case a mixture of two crystalline products is formed: aniline salt and 2-methylethanesulfanilide. The mixture was fractionated either by extraction with ether (in which the salt is poorly soluble) or by direct recrystallization from water (both products dissolve in hot water but only the reaction product comes down on cooling). Two recrystallizations lead to a perfectly pure product.

0.1296 g substance: 6.44 ml 0.1 N H_2SO_4. 0.1263 g substance: 0.1466 g $BaSO_4$. Found %: N 6.95; S 15.91. $C_9H_{13}O_2NS$. Calculated %: N 7.03; S 16.08.

* Strepetova and Sergeeva participated in the experimental work.

** 2-Methylethanesulfochloride was prepared by this method for the first time.

4. Preparation of 2-methylpropanesulfanilide. 4 g 2-methylpropanesulfochloride was reacted with 4.6 g aniline in 20 ml ether. Procedure as above. When the crude reaction product was dissolved in alkali and then precipitated with acid, a crystalline product did not separate but a yellow oil came down which could only be crystallized by very intense cooling and prolonged rubbing with a glass rod. Yield 35% of the theoretical.

0.0980 g substance: 4.5 ml 0.1 N H_2SO_4. 0.1102 g substance: 0.1195 g $BaSO_4$. Found %: N 6.42; S 14.86. $C_{10}H_{15}O_2NS$. Calculated %: N 6.57; S 15.02.

5. Preparation of 2-methylbutanesulfanilide. 2 g 2-methylbutanesulfochloride and 1.8 g aniline were reacted in 40 ml ether. Yield 45% of the theoretical. Reaction without heating in ether gives a yield of 37-38%; in benzene with heating the yield is 34%, without heating it is negligible.

0.0553 g substance: 2.38 ml 0.1 N H_2SO_4. 0.1469 g substance: 0.1500 g $BaSO_4$. Found %: N 6.02; S 14.00. $C_{11}H_{17}O_2NS$. Calculated %: N 6.16; S 14.09.

6. Preparation of methanesulfanisidide. 1.86 g methanesulfochloride and 3 g p-anisidine were reacted in 40 ml ether. The reaction was effected as with aniline. Yield of product 30% of the theoretical.

0.0480 g substance: 2.20 ml 0.1 N H_2SO_4. 0.0891 g substance: 0.1025 g $BaSO_4$. Found %: N 6.41; S 15.77. $C_8H_{11}O_3NS$. Calculated %: N 6.96; S 15.92.

7. Preparation of ethanesulfanisidide. 2 g ethanesulfochloride and 3.8 g p-anisidine were reacted in 40 ml ether. Yield 72% of the theoretical. Reaction in ether at room temperature gives approximately the same yield; in benzene at 60° the yield is 60%, without heating 49%.

0.1390 g substance: 6.50 ml 0.1 N H_2SO_4. 0.1201 g substance: 0.1286 g $BaSO_4$. Found %: N 6.54; S 14.68. $C_9H_{13}O_3NS$. Calculated %: N 6.51; S 14.88.

8. Preparation of 2-methylethanesulfanisidide. 2 g 2-methylethanesulfochloride was reacted with 3.38 g p-anisidine in 40 ml ether. Yield 64% of the theoretical; without heating in ether the yield is 57%. In benzene the yield with heating is 45%. Without a solvent the yield is 37-38%.

0.1223 g substance: 5.31 ml 0.1 N H_2SO_4. 0.1484 g substance: 0.1498 g $BaSO_4$. Found %: N 6.07; S 13.84. $C_{10}H_{15}O_3NS$. Calculated %: N 6.11; S 13.97.

9. Preparation of 2-methylpropanesulfanisidide. 2 g 2-methylpropanesulfochloride and 2.3 g p-anisidine were reacted in 40 ml ether. Yield 30% of the theoretical. Approximately the same yield in ether without heating.

0.0880 g substance: 3.40 ml 0.1 N H_2SO_4. 0.0992 g substance: 0.0960 g $BaSO_4$. Found %: N 5.40; S 13.26. $C_{11}H_{17}O_3NS$. Calculated %: N 5.76; S 13.16.

10. Preparation of 2-methylbutanesulfanisidide. 2 g 2-methylbutanesulfochloride was reacted with 2.8 g p-anisidine in 40 ml ether. With heating the yield of product was 68-69%, without heating 46-47%.

0.0598 g substance: 2.32 ml 0.1 N H_2SO_4. 0.1354 g substance: 0.1221 g $BaSO_4$. Found %: N 5.43; S 12.36. $C_{12}H_{19}O_3NS$. Calculated %: N 5.44; S 12.45.

11. Preparation of ethanesulfophenetidide. 2 g ethanesulfochloride was reacted with 4.2 g p-phenetidine in 40 ml ether. Yield 80% of the theoretical

0.1036 g substance: 4.56 ml 0.1 N H_2SO_4. Found %: N 6.16. $C_{10}H_{15}O_3NS$. Calculated %: N 6.11.

The sulfur was not determined in this compound.

12. Preparation of 2-methylethanesulfophenetidide. 1.42 g 2-methylethanesulfochloride and 2.74 g p-phenetidine were reacted in 40 ml ether. With heating the yield was 75% of the theoretical, without heating 53-54%. In benzene with heating the yield was 49.5%, without heating 45.5%; without a solvent the yield was 65.8%.

0.1209 g substance: 4.93 ml 0.1 N H_2SO_4. 0.1644 g substance: 0.1581 g $BaSO_4$. Found %: N 5.70; S 13.18. $C_{11}H_{17}O_3NS$. Calculated %: N 5.76; S 13.16.

All the compounds prepared were fairly resistant to hydrolysis. They were recovered unchanged after boiling for 10-15 minutes with water, dilute alkali and dilute acid.

SUMMARY

1. Reactions of alkanesulfochlorides with aniline, p-anisidine and p-phenetidine have been studied.

2. Preparation and characterization were carried out of the anilides, and p-anisidides of methane-, ethane-, 2-methylpropane-, and 2-methylbutanesulfonic acids, and of the p-phenetidides of ethane- and 2-methylethanesulfonic acids.

3. The reactions of alkanesulfochlorides with amines can be applied to the separation of primary and secondary amines.

4. The preparation of anilides, anisidides and phenetidides can be utilized for identification of alkanesulfonic acids.

LITERATURE CITED

[1] A. G. Kostsova, J. Gen. Chem. 11, 63 (1941); J. Gen. Chem. 18, 730 (1948); J. Gen. Chem. 19, 346 (1949); see Consultants Bureau translation, p. 307.

[2] N. I. Melnikov, Sukhareva and Kavenoki, J. Appl. Chem. USSR, 18, 568 (1945).

[3] A. G. Kostsova, Trans. Voronezh State Univ., 8, 93 (1935).

[4] A. Ya. Yakubovich and Yu. M. Zinovev, Prog. Chem. 16, 581 (1947).

[5] Latimer, Bost, J. Org. Chem. 5, 24 (1940).

[6] R. Shriner, M. Goebel, J. Am. Chem. Soc. 54, 2470 (1932).

[7] Houben, Vol. II, part 3, 563.

Received April 17, 1950

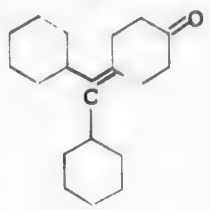
Voronezh State University

HYDROXYFUCHSONE DYES

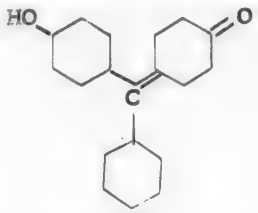
XVI [1]. 2-HYDROXYFUCHSONE

I. S. Ioffe and B. G. Belenky

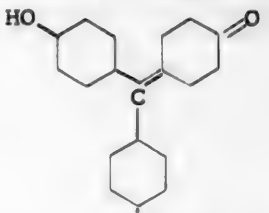
Of the hydroxy derivatives of fuchsone (I) only benzaurin (II) [2] and aurin (III) [2], containing hydroxyl groups in the p-positions of one or both benzene rings of the fuchsone complex, have been at all closely investigated.



(I)

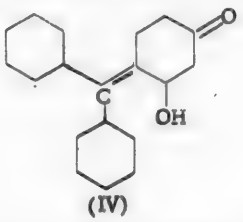


(II)

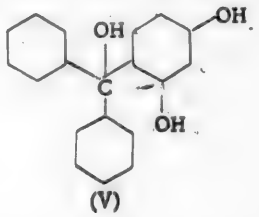


(III)

It has been established that the various properties of hydroxyfuchsone dyes, their color [4], stability of their hydrochlorides [5], their relations with corresponding carbinol derivatives [5], etc. depend on the number of hydroxyl groups. With the aim of investigating the influence of the position of the hydroxyl groups, we decided to compare benzaurin (II) with the isomeric 2-hydroxyfuchsone (IV) which contain the hydroxyl group not at a benzene nucleus but at the quinoid nucleus of the fuchsone complex:



(IV)

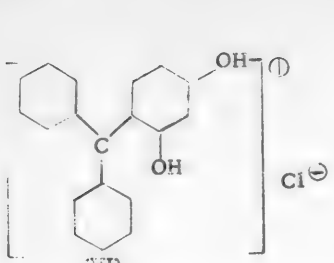


(V)

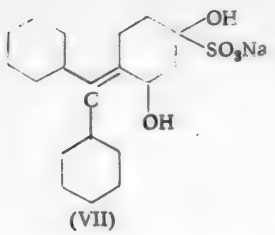
The corresponding carbinol derivative, 2,4-dihydroxytriphenylcarbinol (V), has already been described by Bayer [6] who prepared it by condensing phenyl magnesium bromide with 2,4-dihydroxybenzophenone. By this route, however, the yield of carbinol (V) is very low, and great difficulties are met with in the separation and purification of this compound. We applied the method of condensation of benzophenone chloride with resorcinol to the preparation of 2-hydroxyfuchsone and its corresponding carbinol. This general method of preparation, proposed by Gomberg and Jickling [7], was applied and somewhat improved in our laboratory [8] for the preparation of both fuchsone itself and 3-methoxyfuchsone.

Qualitative experiments showed that the condensation of benzophenone chloride with resorcinol proceeds very rapidly, much more rapidly than with phenol or guaiacol. In view, however, of the high melting point of resorcinol, the condensation is better conducted in an organic solvent, the most suitable being glacial acetic acid. By this means not only is the condensation of benzophenone chloride with resorcinol itself speeded up but the isolation is facilitated of the condensation product which generally has a low stability and decomposes when heated. For the latter reason a low reaction temperature is also preferable. The color changes to crimson during the process due to the formation of 2-hydroxyfuchsone hydrochloride, an onium salt with structure (VI): (see top of next page).

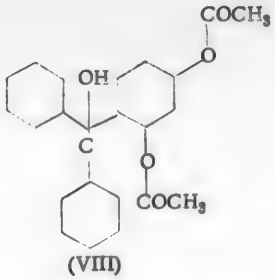
As was confirmed by further experiments with an existing pure preparation, this salt readily hydrolyzes, and when heated it decomposes to form benzophenone; in order to isolate it from the reaction mass, we therefore used a method based on preparation of the bisulfite derivative, which had been successfully used in our laboratory [8] for the preparation of fuchsone and 3-methoxyfuchsone.



(VI)



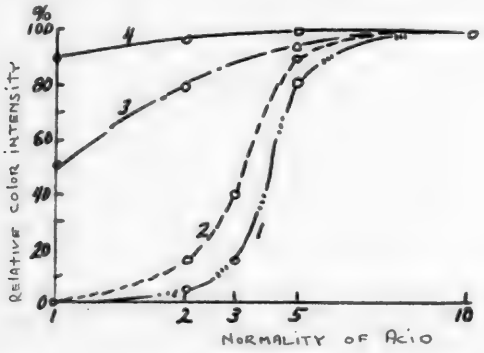
(VII)



(VIII)

The bisulfite compound, to which on the basis of previous studies [9] we ascribe the structure (VII), is obtained by direct treatment of the reaction mixture with an aqueous solution of sodium bisulfite. It forms colorless crystals, easily purified by crystallization from water. The aqueous solutions of the bisulfite derivative turn yellow when heated, but the color disappears on cooling or on addition of bisulfite; this behavior suggests the presence of a labile equilibrium between the fuchsone derivative and its bisulfite compound. By careful treatment of the reaction mass under the optimum conditions described below, the bisulfite derivative of 2-hydroxyfuchsone can be obtained pure in a yield close to the theoretical, calculated on the original chlorobenzophenone.

The pure hydrochloride of 2-hydroxyfuchsone (VI) was prepared from the bisulfite compound by the action of hydrochloric acid. It is a crystalline powder with a red color, melting (in a rapid melting point determination) at 105-107°. Even at 80-85°, however, the color begins to darken and hydrochloric acid is evolved, indicating dissociation of the hydrochloride. This dissociation also proceeds, although very much slower, when the preparation is kept in an open vessel at room temperature.



Colorimetric evaluation of the degree of hydrolysis of salts of fuchsone (I), 2-hydroxyfuchsone (2), benzaurin (3), and aurin (4) in hydrochloric acid solutions of various strengths.

The stability of 2-hydroxyfuchsone hydrochloride is also very low in aqueous solutions, the latter undergoing hydrolysis with relative ease. Salts of other hydroxyfuchsones are much more resistant to hydrolysis. In one of the previous communications [5] results were described of comparative colorimetric determinations of various hydroxyfuchsones when it was shown that resistance to hydrolysis increases with increasing number of hydroxyl groups. Thus, for example, in 1 N hydrochloric acid the salt of aurin is only hydrolyzed to the extent of 10%, that of benzaurin to the extent of 50%, while fuchsone (containing no hydroxyl groups) is nearly completely hydrolyzed. It was found, however, that resistance to hydrolysis depends not only on the number of hydroxyl groups but also on their position. The salt of 2-hydroxyfuchsone, isomeric with benzaurin but containing the hydroxyl group not at the benzene ring but at the quinoid ring, resembles not the salt of benzaurin but that of fuchsone (which does not contain a hydroxyl group) in its ease of hydrolysis, being hydrolyzed almost completely in 1 N hydrochloric acid. In the accompanying diagram are plotted the curves characterizing the degree of hydrolysis of the salts of fuchsone, 2-hydroxyfuchsone, 4'-hydroxyfuchsone (benzaurin) and 4',4"-dihydroxyfuchsone (aurin) in solutions of hydrochloric acid with strengths ranging from 1 N to 10 N.

This diagram clearly demonstrates that in respect of stability of the salts to hydrolysis, 2-hydroxyfuchsone is very much closer to fuchsone than to benzaurin or aurin.

2-Hydroxyfuchsone also resembles unsubstituted fuchsone more closely in respect of ease of transformation into the corresponding carbinol derivative. As already pointed out [10], fuchsones and their carbinols are in a state of labile equilibrium. The ease of hydration of fuchsones depends, however, on the number of hydroxyl groups in

para-positions of the benzene rings of the fuchsone complex. Aurin and benzaurin undergo complete conversion to the carbinols when in an alkaline medium. With sufficiently high alkali concentration, the initially formed colored alkaline salts are completely converted into the colorless salts of the carbinols. Solutions of aurin are completely decolorized at a pH exceeding 12; solutions of benzaurin at a pH exceeding 10. But fuchsones not containing hydroxyl groups are hydrated even in a neutral medium, even if dissolved in an organic solvent to which water is added. It was found that the susceptibility of 2-hydroxyfuchsone to hydration in neutral solutions is as great as, if not greater than, that of fuchsone. Consequently the hydrolysis of acid-onium salts of aurin and benzaurin yields free dyes. Hydrolysis of similar salts of fuchsone yields a mixture of fuchsone itself and 4-hydroxytriphenylcarbinol [11]. Hydrolysis of the acid-onium salt of 2-hydroxyfuchsone results, however, in nearly complete formation of the carbinol derivative, 2,4-dihydroxytriphenylcarbinol (V).

Thanks to this behavior we were able to effect the preparation of 2,4-dihydroxytriphenylcarbinol (V) far more easily and with a very much greater yield than achieved by Bayer [6]. On triturating 2-hydroxyfuchsone hydrochloride with water, or better with sodium acetate solution, a colorless flocculent precipitate of 2,4-dihydroxytriphenylcarbinol is formed. The latter is converted by heating into 2-hydroxyfuchsone, so that the crystallization of 2,4-dihydroxytriphenylcarbinol must be performed very carefully with avoidance of excessive heating. The best procedure for crystallization is to dissolve the substance in benzene containing a trace of water and to heat to 60°. On slow cooling the carbinol separates in the form of colorless crystals. During the melting point determination the crystals gradually turn yellow, but in a rapid melting point determination they melt sharply at 124-125°.

The stability of 2,4-dihydroxytriphenylcarbinol is low. When heated it dehydrates to form 2-hydroxyfuchsone. When treated with hydrochloric acid it forms the hydrochloride of 2-hydroxyfuchsone. 2,4-Dihydroxyfuchsone is soluble in alkali, but the solution gradually turns cloudy, more rapidly on heating, due to formation of benzophenone. The latter collects in oily drops which solidify on standing.

2-Hydroxyfuchsone is likewise very unstable. It hydrates very easily, and when heated it decomposes with formation of benzophenone; we were consequently unable to isolate 2-hydroxyfuchsone in the analytically pure form. When heated in glacial acetic acid, 2,4-dihydroxytriphenylcarbinol forms an orange solution of 2-hydroxyfuchsone, but addition of water to the same solution leads to the reverse process of hydration with formation of a mixture of fuchsone and the carbinol. Heating of the 2,4-dihydroxytriphenylcarbinol with acetic acid followed by vacuum distillation of the solvent results in partial decomposition of the fuchsone. Partial decomposition also takes place when 2,4-dihydroxytriphenylcarbinol is dehydrated in the absence of a solvent in vacuum without heating; in our investigation we therefore isolated 2-hydroxyfuchsone in the form of its more stable hydrochloride or bisulfite compound.

From 2,4-dihydroxytriphenylcarbinol we also prepared its diacetyl derivative (VIII). This is more stable, and after crystallization from benzene it is obtained as colorless crystals melting sharply at 178-180°. The same acetyl derivative is obtained from 2-hydroxyfuchsone hydrochloride by heating with acetic anhydride and anhydrous sodium acetate, or from free 2-hydroxyfuchsone by heating with acetic anhydride. In the latter case, however, the purification of the acetyl derivative calls for several recrystallizations, because, for the reasons indicated above, 2-hydroxyfuchsone itself is contaminated with products of its own decomposition.

Investigation of 2-hydroxyfuchsone and its derivatives, and a comparison of them with aurin and benzaurin, show that the properties of hydroxyfuchsone derivatives essentially depend not only on the presence of hydroxyl groups and their number but also on their position.

The presence of hydroxyl groups in the p-positions of the benzene rings of the fuchsone grouping results in greater stability of the acid-onium salts of hydroxyfuchsone dyes. Apart from that, such hydroxyfuchsone dyes are more stable in the free state and undergo hydration only in a strongly alkaline medium with formation of colorless carbinol derivatives. 2-Hydroxyfuchsone, which contains the hydroxyl group in the quinoid ring in the o-position to the central carbon atom of the fuchsone complex, more closely resembles fuchsone (free from hydroxyl groups) in respect of stability of the acid-onium salt; moreover, 2-hydroxyfuchsone is very susceptible to hydration and therefore, unlike aurin or benzaurin, dissolves in dilute alkali to give the colored salt of hydroxyfuchsone and the colorless salt of the corresponding carbinol. In a neutral medium 2-hydroxyfuchsone also hydrates even more easily than the unsubstituted fuchsone.

From the foregoing considerations it follows that the hydroxyl group in the 2-position of the quinoid ring differs markedly from the hydroxyl group in the p-position of the benzene rings in its influence on the properties of hydroxyfuchsones. A possible reason for this is the development of a hydrogen bond with a blocking effect

between the hydroxyl group in the 2-position and the neutral carbon atom.

EXPERIMENTAL

Bisulfite compound of 2-hydroxyfuchsone. 11 g resorcinol is dissolved in 15 ml glacial acetic acid and to the solution is added, with cooling, 16.5 g freshly distilled benzophenone chloride. The vessel is closed with a stopper fitted with an elongated capillary and left to stand in a cold place for 2 days. The reaction proceeds with evolution of hydrochloric acid. The reaction mixture thickens and acquires a crimson color much darker than the color of solutions of benzaurin hydrochloride.

To the resultant reaction mixture is added 50 ml saturated solution of sodium bisulfite and 200 ml 15% sodium chloride solution. This mixture is heated to the boil and after addition of 1-2 g animal charcoal it is filtered. Cooling results in separation of a crystalline precipitate of the colorless bisulfite compound of 2-hydroxyfuchsone. The precipitate is filtered, washed with a little cold water and purified by recrystallization from water. Yield 25 g.

The bisulfite compound of 2-hydroxyfuchsone crystallizes from water in colorless crystals containing 1.5 moles water of crystallization. After dehydration it melts at 193-195° with decomposition. It is readily soluble in water and almost insoluble in organic solvents. The aqueous solutions turn yellow when heated, and when diluted with water a milky-white turbidity is formed due to hydrolysis of the bisulfite compound and hydration of the resultant fuchsone to the corresponding carbinol. Reaction with hydrochloric acid gives 2-hydroxyfuchsone hydrochloride.

The water of crystallization and the sodium content were determined on the substance dried to constant weight in the desiccator.

0.4879 g substance: 0.0308 g H_2O. 0.7955 g substance: 0.1390 g Na_2SO_4. 6.9196 g substance: 0.1582 g Na_2SO_4. Found %: H_2O 6.31; Na 5.66, 5.57. $C_{19}H_{17}O_3NaHSO_3 \cdot 1\frac{1}{2} H_2O$. Calculated %: H_2O 6.66; Na 5.68.

2-Hydroxyfuchsone hydrochloride. 25 g bisulfite derivative is dissolved in 150 ml water and impurities are filtered off. The filtrate is cooled and addition is made, with intensive stirring and external cooling, of 150 ml strong hydrochloric acid. The dark-red flocculent precipitate is filtered, well pressed, and washed with 15% hydrochloric acid solution. The precipitate is dried under vacuum and stored in a vacuum desiccator over calcium chloride. Yield 20 g.

Properties: Deep-scarlet crystalline powder, m.p. in a normal determination 105-107°. On slow heating gas is evolved and the color deepens at 80-85°. In water it rapidly hydrolyzes with simultaneous hydration. It dissolves with a crimson color in glacial acetic acid, amyl acetate, and ether. When traces of water are present in the solvents, decolorization takes place due to hydrolysis and hydration. When heated in hydrochloric acid it decomposes with formation of benzophenone.

Resistance to hydrolysis: 0.01 g substance is dissolved in 10 ml alcohol. To 0.1 ml portions of the solution are added lots of 10 ml hydrochloric acid with normalities of 11, 5, 3, 2 and 1.

Similar experiments were carried out for comparison with aurin, benzaurin, and fuchsone. After standing for one hour for attainment of equilibrium, colorimetric determinations were made of the color intensities which characterized the content of nonhydrolyzed hydrochloride. A solution in 10 N acid was used as standard. The results are presented in the table.

2,4-Dihydroxytriphenylcarbinol. 18 g bisulfite compound of 2-hydroxyfuchsone is dissolved in 150 ml hot water. After cooling, addition is made to the solution, with intensive stirring, of 150 ml concentrated hydrochloric acid. The precipitate of hydrochloride is filtered, washed with 15% hydrochloric acid and then transferred to a porcelain mortar in which is introduced 15 g sodium acetate and a little water. A resinous brown mass is formed which on trituration gradually whitens and subsequently changes into a viscous homogeneous suspension. This is transferred to a beaker, 150 ml water is added and the whole left for 24 hours in the cold. The bright precipitate of carbinol is filtered and washed with water. Without being dried, the product is put into benzene and warmed to 70°; the benzene layer is poured off from the aqueous layer through an ordinary filter. Cooling of the benzene solution brings out colorless crystals of 2,4-dihydroxytriphenylcarbinol; these are filtered and dried in a vacuum desiccator. Yield 8.7 g (67% of the theoretical).

Properties: Colorless or slightly yellow crystals with m.p. 123-124° (on rapid determination). Slow heating

to 75-80° results in marked darkening and softening due to the transformation into 2-hydroxyfuchsone. It is soluble in alcohol, ether, chloroform and hot benzene, almost insoluble in water, gasoline and petroleum ether. When treated with strong hydrochloric acid it is converted into the salt of 2-hydroxyfuchsone. Heating with glacial acetic acid gives an orange solution of 2-hydroxyfuchsone. The latter is also obtained by heating the carbinol above 80°. On heating with alkali it decomposes with formation of benzophenone.

Color Intensity of Hydrochlorides of some Hydroxyfuchsone Dyes

Dye	Normality of HCl				
	10	5	3	2	1
Aurin	100	100	–	–	90
Benzaurin	100	95	–	80	50
2-Hydroxyfuchsone	100	90	40	15	0
Fuchsone	100	80	15	5	0

0.0872 g substance*. 0.2509 g CO_2; 0.0437 g H_2O. 0.0831 g substance: 0.2592 g CO_2; 0.0452 g H_2O. 0.0970 g substance: 6.8 ml 0.1 N NaOH. 0.1228 g substance: 8.5 ml 0.1 N NaOH.* Found %: C 78.52, 78.55; H 5.61, 5.28; (OH) 11.92, 11.77. $C_{19}H_{16}O_3$. Calculated %: C 78.08; H 5.48; (OH) 11.65.

2,4-Diacetoxytriphenylcarbinol. 30 g 2,4-dihydroxytriphenylcarbinol is boiled with 30 ml acetic anhydride. After dissolving, the carbinol solution develops an orange color which gradually lightens. Heating for an hour results in a light-yellow solution which is poured into 200 ml water. With progressive decomposition of the acetic anhydride the acetyl derivative separates in the form of clots which are filtered, washed with water and crystallized from benzene. Yield almost quantitative.

The colorless crystals melt sharply at 178-180°. Soluble in benzene and glacial acetic acid; insoluble in water. Relatively stable when treated with hydrochloric acid. With hydrochloric acid the substance saponifies in solution in glacial acetic acid with formation of 2-hydroxyfuchsone hydrochloride. It is saponified by heating with alkali but this process is accompanied by decomposition of the resultant 2,4-dihydroxytriphenylcarbinol.

0.0861 g substance: 0.2319 g CO_2; 0.0422 g H_2O. 0.0758 g substance: 0.2045 g CO_2; 0.0366 g H_2O. Found %: C 73.50, 73.62; H 5.48, 5.40. $C_{23}H_{18}O_5$. Calculated %: C 73.40; H 5.32.

SUMMARY

2-Hydroxyfuchsone can be prepared by condensation of benzophenone chloride with resorcinol; this reaction gives 2-hydroxyfuchsone hydrochloride. For the purpose of isolation and purification it is more convenient to prepare the bisulfite compound, from which the pure hydrochloride can be obtained by treatment with strong hydrochloric acid.

2-Hydroxyfuchsone only forms acid salts. It rapidly hydrates when treated with alkali to form the salt of 2,4-dihydroxytriphenylcarbinol. This carbinol derivative is also formed by hydration of 2-hydroxyfuchsone also in a neutral medium, as well as on hydrolysis of the hydrochloride.

The hydrochloride is only stable in concentrated solutions of strong acids. On addition of water the salt hydrolyzes more easily than the salt of hydroxyfuchsone dyes containing hydroxyl groups in the para-positions of the benzene rings of the fuchsone grouping (benzaurin and aurin). In contrast to the latter, hydrolysis of the hydrochloride is accompanied by hydration.

Acetylation of 2-hydroxyfuchsone and 2,4-dihydroxytriphenylcarbinol results in formation of 2,4-diacetoxytriphenylcarbinol.

2-Hydroxyfuchsone is unstable in storage. It readily hydrolyzes, and when heated it splits up with formation of benzophenone. 2-Hydroxyfuchsone can be kept in the form of its hydrochloride or, better still, in the form of its bisulfite compound.

A compound of 2-hydroxyfuchsone with benzaurin or aurin shows that in 2-hydroxyfuchsone the hydroxyl group on the quinoid nucleus in the o-position to the central carbon atom of the fuchsone grouping appears to be blocked, possibly due to a hydrogen bond.

LITERATURE CITED

[1] I. S. Ioffe, J. Gen. Chem., 21, 1677 (1951); see Consultants Bureau translation, p. 1655.

* Difference between direct and back titration on acetylation.

[2] O. Doebner, Ann. 217, 230 (1883).

[3] R. C. Dahle and C. Schorlemmer, Ann., 166, 286 (1873).

[4] I. S. Ioffe and A. F. Sukhina, J. Gen. Chem. 19, 1169 (1949).*

[5] I. S. Ioffe, J. Gen. Chem. 17, 1904 (1947).

[6] A. Bayer, Ann., 372, 80 (1910).

[7] M. Gomberg and R. Yickling, J. Am. Chem. Soc. 37, 2575 (1915).

[8] I. S. Ioffe and Z. Ya. Khavin, J. Gen. Chem. 19, 917 (1949).**

[9] I. S. Ioffe, J. Gen. Chem. 19, 911 (1949). ***

[10] I. S. Ioffe, J. Gen. Chem. 20, 346 (1950). ****

[11] I. S. Ioffe and Z. Ya. Khavin, J. Gen. Chem. 20, 158 (1950). *****

Received December 15, 1950

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* See Consultants Bureau translation, p. 1169.

** See Consultants Bureau translation, p. 903.

*** See Consultants Bureau translation, p. 897.

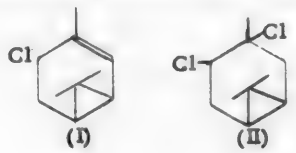
**** See Consultants Bureau translation, p. 367.

***** See Consultants Bureau translation, p. 161.

dΔ³-CARENE DICHLORIDE

B. A. Arbuzov and V. A. Frinovskaya

In a series of interesting papers recently published by D. V. Tishchenko and co-workers [1,2], a study was made of the action of chlorine on terpene hydrocarbons in presence of hydrogen chloride-binding substances. In the reaction of chlorine with dΔ³-carene in presence of sodium bicarbonate, D. V. Tishchenko and A. Khovanskaya [3] isolated from the reaction products an unsaturated monochloride and a dichloride; the latter could not be isolated in the pure form. The authors ascribe structure (I) to the monochloride. They do not give any data for the structure of the dichloride.



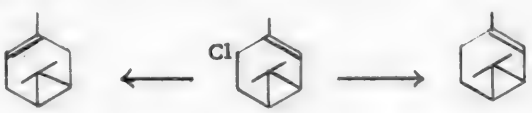
(I) (II)

Recently we have also studied the action of chlorine on terpene hydrocarbons in presence of hydrogen chloride-binding materials. In the chlorination of dΔ³-carene we isolated, apart from the monochloride, a dichloride in a purer form than was got by Tishchenko and Khovanskaya, and we determined its structure by reconversion to carene with the aid of finely divided sodium as a chlorine-binder. The so-prepared hydrocarbon gave a nitrosate with m.p. 143.5-144.0°, identical with the nitrosate of dΔ³-carene, and in the same yields as from pure dΔ³-carene. The preparation of dΔ³-carene from the dichloride indicates that the latter has the structure (II)

The unsaturated monochloride separated from the products of chlorination has constants fairly close to those reported by Tishchenko and Khovanskaya. Reduction of the monochloride with sodium in methyl alcohol at a temperature not exceeding 50° [4] gave a hydrocarbon which was not perfectly pure but whose constants were close to those of dΔ³-carene.

Fractions of the hydrocarbon gave good yields of the nitrosate of dΔ³-carene with m.p. 143.5-144.5°, indicating the presence of considerable amounts of Δ³-carene.

The formation of Δ³-carene by reduction of the monochloride is not inconsistent with the formula (I) proposed by Tishchenko and Khovanskaya since the reduction of allyl chlorides by metals in alcohol is accompanied by an allyl rearrangement [5], and in the case of reduction of monochloride (I) we should expect the formation of Δ³- and Δ⁴-carenes



which could not be separated by fractionation due to the closeness of the boiling points.

EXPERIMENTAL

dΔ³-Carene was separated from sulfate turpentine by fractionation in a column with 25 theoretical plates and had the constants: b.p. 63° (7 mm); d_0^{20} 0.8615; n_D^{20} 1.4729.

285 g Δ³-carene and 120 g sodium carbonate were mixed in a three-necked flask provided with a mechanical stirrer and immersed in freezing mixture (ice and salt). A slow stream of dry chlorine was passed through the Δ³-carene for 12 hours. After separation of the bicarbonate and the sodium chloride, the filtrate consisted of an aqueous layer (38.3 g) and an oil (315 g). Fractionation of the oil in vacuum using a Widmer dephlegmator yielded the following fractions (10 mm):

1) 49-69°, 75 g; 2) 59-80°, 52.5 g; 3) 80-84°, 26.7 g; 4) 84-85°, 28 g; 5) 85-120°, 70 g; 6) 120-153°, 29.2 g; residue 13 g.

Redistillation of the second to fourth fractions gave fractions with the following constants:

1) 72-74° (7 mm), 18 g; n_D^{20} 1.5028; d_0^{20} 0.9826; 2) 74-76° (7 mm), 37.2 g; n_D^{20} 1.5026; d_0^{20} 1.0047; MR_D 49.78. $C_{10}H_{15}Cl$ (three-membered ring); calculated 48.99.

0.1770 g substance: 0.1444 g AgCl. 0.1420 g substance: 0.01281 g active oxygen,* 0.1860 g substance: 0.01667 g active oxygen.* Found%: Cl 20.18; double bonds 0.96, 0.95. $C_{10}H_{15}Cl$. Calculated %: Cl 20.82.

Reduction of the monochloride with sodium. 15 g monochloride in 200 ml absolute methyl alcohol was reduced by addition of sodium (20 g), care being taken that the temperature of the liquid did not rise above 50°. After the whole of the sodium had been added, an extra 50 ml methyl alcohol was added, and the whole poured into water and extracted with ether; the residue after removal of the ether was distilled. After three distillations the following fractions (7 mm) were obtained:

1) 50-54°, 7.5 g; 2) 54-74°, 1 g; 3) 74-75°, 2.3 g.

The first fraction was distilled over sodium to give (7 mm):

a) 42-46°; n_D^{20} 1.4700; d_0^{20} 0.8634, 1.2 g; b) 46-50°; n_D^{20} 1.4712; d_0^{20} 0.8572, 3.2 g; c) 50-58°; n_D^{20} 1.4738; d_0^{20} 0.8692, 2.5 g.

From all three fractions the nitrosate of Δ^3-carene (m.p. 143.5-144.5° without recrystallization) was prepared.

The third fraction with b.p. 74-75° (7 mm) contained 3.9% chlorine. It was again reduced with sodium in methyl alcohol and had: b.p. 62-68° (6 mm); n_D^{20} 1.4760; d_0^{20} 0.9029.

Isolation of carene dichloride. Fractions 5-6 of the product of chlorination of Δ^3-carene gave after fractionation a fraction (36 g) with b.p. 107-110° (7 mm); n_D^{20} 1.5052; d_0^{20} 1.1146; MR_D 55.11. $C_{10}H_{16}Cl_2$ (three-membered ring); calculated 54.32.

0.1392 g substance: 0.1918 g AgCl. Found %: Cl 34.12. $C_{10}H_{16}Cl_2$. Calculated %: Cl 34.3. Titration with perphthalic acid showed the absence of double bonds.

Regeneration of Δ^3-carene from the dichloride. 15 g metallic sodium was pulverized to dust in hot toluene. To the cooled toluene was carefully added 20 g dichloride. Considerable heat was developed and the reaction continued for 2.5 hours; after decantation and distillation of the toluene in vacuum the residue was distilled. B.p. 44-50° (7 mm); 6.8 g. The following fractions were obtained by distillation (7 mm):

1) 40-45°, 1.2 g and 2) 45-48°, 4.3 g; n_D^{20} 1.4755; d_0^{20} 0.8639; MR_D 44.29; calculated 44.13.

The second fraction (2.5 g) yielded, by Simonsen's method, 0.4 g nitrosate with m.p. 143.5-144.0 without recrystallization. Parallel preparation of nitrosate from pure Δ^3-carene yielded (from 2.5 g) 0.5 g nitrosate.

SUMMARY

1. The dichloride prepared by chlorination of dΔ^3-carene by D. V. Tishchenko's method is 3,4-dichlorocarane, since cleavage of chlorine with sodium gives Δ^3-carene.

2. Reduction with sodium in alcohol of the unsaturated monochloride obtained from dΔ^3-carene gives a mixture of Δ^3-carene and, apparently, Δ^4-carene, and the process is accompanied by an allyl rearrangement.

LITERATURE CITED

[1] D. V. Tishchenko, J. Gen. Chem. 20, 563 (1950).**

[2] D. Tishchenko and T. Danilov, J. Gen. Chem. 20, 998 (1950).***

[3] D. V. Tishchenko and A. Khovanskaya, J. Gen. Chem. 20, 1003 (1950).****

[4] I. I. Bardyshev, A. Piryatinsky, K. Bardysheva and O. Chernyaeva, J. Appl. Chem. USSR 23, 657 (1950).*****

[5] E. W. Semmler, Ber., 41, 4478 (1908).

[6] W. G. Joung, N. Kaufman, A. Loshokoff and D. Pressman, J. Am. Chem. Soc. 60, 900 (1938).

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Received December 5, 1950

* Titration with perphthalic acid.

** See Consultants Bureau translation, p. 593.

*** See Consultants Bureau translation, p. 1037.

**** See Consultants Bureau translation, p. 1043.

***** See Consultants Bureau translation, p. 693.

NITRATION OF (1,2,3,4)-TETRAHYDRO-2-NAPHTHOIC ACID

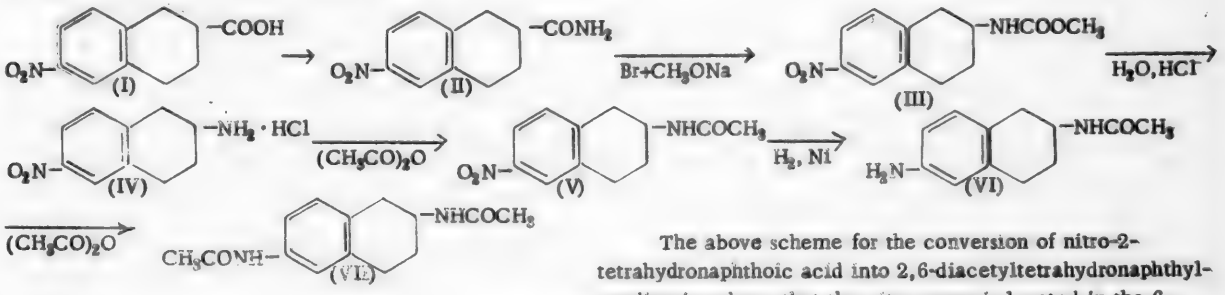
S. I. Sergievskaya and N. P. Volynsky

The presence of a substituent in the 2-position of the hydrogenated portion of the tetrahydronaphthalene molecule so changes the chemical properties of its nonhydrogenated ring that the usual reactions of aromatic compounds, such as nitration, proceed with extraordinary difficulty or entirely fail to give the anticipated results. It suffices to mention the repeated and unsuccessful efforts to nitrate the well-known ac-β-tetrahydronaphthylamine, or the difficulty in nitrating β-tetralone. In this investigation we have applied the nitration reaction to ac-2-tetrahydronaphthoic acid; using nitric acid of s.g. 1.5, no clear results were obtained, but by nitration with acid of s.g. 1.4-1.42 we succeeded in isolating a crystalline substance of acidic nature with m. pt. 196.5-197°. The yield, however, did not exceed 10%, the greater part of the ac-β-tetrahydronaphthoic acid being converted into a difficultly separable mixture of oily substances which we did not examine more closely.

The elementary analysis of the crystalline compound with m.pt. 196.5-197° showed it to correspond to a mononitrotetrahydronaphthoic acid, and its transformations (formation of an acid chloride, amide, ethyl ester, and – by catalytic reduction – aminotetrahydronaphthoic acid) confirmed the presence of both a carboxyl and a nitro group.

A preliminary determination of the position of the nitro group was made by decarboxylation of the aminotetrahydronaphthoic acid obtained from the nitro acid by the route indicated above. Decarboxylation was performed by dry distillation of the amino acid with barium hydrate at atmospheric pressure; the sole reaction product was β-naphthylamine since decarboxylation was accompanied by dehydrogenation of the tetrahydronaphthalene ring. These results established that the amino group (and consequently the nitro group) is in the 6- or 7- position of tetrahydronaphthalene.

The position of the nitro group was definitely established by the following transformations: The amide of nitrotetrahydro-2-naphthoic acid (II) was converted into the corresponding urethane (III) by the action of bromine and sodium methylate; without purification, (III) was subjected to saponification with the help of concentrated hydrochloric acid. These reactions yielded the hydrochloride of nitro-ac-2-tetrahydronaphthylamine (IV), not previously described in the literature; this nitroamine was converted into its acetyl derivative (V), and the nitro group in the latter was reduced to the amino group (VI). Acetylation of the resultant compound yielded the known, 2,6-diacetyltetrahydronaphthylenediamine (VII) [1]:



The above scheme for the conversion of nitro-2-tetrahydronaphthoic acid into 2,6-diacetyltetrahydronaphthylenediamine shows that the nitro group is located in the 6-position of the tetrahydronaphthalene ring and the nitro acid which we have prepared is 6-nitro-(1,2,3,4)-tetrahydro-2-naphthoic acid (I).

EXPERIMENTAL

6-Nitro-ac-tetrahydro-2-naphthoic acid. 70 g ac-tetrahydro-2-naphthoic acid with m. pt. 90-92° is added in one portion to 350 ml HNO_3, s.g. 1.42 and the mixture is heated (to initiate the reaction) to 38-40°, after which this tem-

perature is maintained for two hours. At the conclusion of the reaction the solution is cooled to −5° and the resultant precipitate is filtered off. Yield 13.5 g with m. pt. 175-180°. The filtrate is heavily diluted with water which precipitates a yellow resin; the latter is separated from the aqueous acid solution and triturated with toluene. The insoluble precipitate is filtered off, giving a further 5 g of substance with m. pt. 175-185°. Nitration by the above-described method (in two lots) of 185 g ac-tetrahydro-2-naphthoic acid with m. pt. 90-92° gave 30 g of substance with m. pt. 170-180°, which separated from the reaction mixture and 20 g substance with m. pt. 150-170° which separated on diluting the acid solution with water.

The 20 g substance with m. pt. 150-170° was recrystallized from toluene to give 15 g nitro acid with m. pt. 188-191° (I). The toluene mother liquor yielded (after distilling off the toluene) 3 g of substance with m. pt. 160-215°.

The 30 g of substance with m. pt. 170-180° was also recrystallized from toluene. Yield 24 g with m. pt. 178-188° (II).

The 24 g of (II) was dissolved in 10% sodium carbonate solution and fractionally precipitated with hydrochloric acid, giving 15 g with m. pt. 178-190° (first fraction) and 9 g with melting point 175-215° (second fraction). The first fraction was recrystallized from alcohol to give a yellowish substance with m. pt. 190-193°. The substance with m. pt. 190-193° was combined with substance (I) with m. pt. 188-191° and twice recrystallized from alcohol. There was obtained 22 g 6-nitro-ac-tetrahydro-2-naphthoic acid with m. pt. 196.5-197°. It was in the form of light-yellow crystals readily soluble in ether, acetone and (with heating) alcohol, less easily soluble in hot toluene, very sparingly soluble in alcohol and toluene in the cold

6.675 mg substance: 0.386 ml N_2 (21.5°, 721.0 mm). 4.069 mg substance: 8.965 mg CO_2; 1.851 mg H_2O. Found %: N 6.36; C 60.09; H 5.09. $C_{11}H_{11}O_4N$. Calculated %: N 6.34; C 59.74; H 4.97.

Ethyl ester of 6-nitro-ac-tetrahydro-2-naphthoic acid. 1 g of 6-nitro-ac-tetrahydro-2-naphthoic acid is heated with 15 ml absolute ethyl alcohol and 3 drops concentrated H_2SO_4 at the boiling point for 6 hours. A bulky crystalline precipitate comes down on cooling and is filtered at the pump and washed with a small amount of absolute alcohol. Yield 1 g substance with m. pt. 83°. After recrystallization from absolute alcohol the ethyl ester of 6-nitro-ac-tetrahydro-2-naphthoic acid forms silky, colorless needles with m. pt. 83.5-84°. Readily soluble in acetone, ether, benzene, hot ethyl alcohol; very sparingly soluble in cold ethyl alcohol.

5.410 mg substance: 0.284 ml N_2 (22.0°, 721.0 mm). Found %: N 5.75. $C_{13}H_{15}O_4N$. Calculated %: N 5.62.

6-Nitro-ac-tetrahydro-2-naphthoyl chloride. 1 g 6-nitro-ac-tetrahydro-2-naphthoic acid is heated with 4 ml $SOCl_2$ at 85-90° for 3 hours, after which the excess of thionyl chloride is removed in vacuum and the residue recrystallized from CCl_4. The acid chloride forms colorless needles with m. pt. 113-113.5°, readily soluble in benzene, acetone and CCl_4 (hot), very sparingly soluble in petroleum ether and cold CCl_4.

6-Nitro-ac-tetrahydro-2-naphthoic acid amide. 7 g 6 nitro-ac-tetrahydro-2-naphthoyl chloride is dissolved in absolute benzene and the solution is shaken with strong aqueous ammonia solution. The precipitate of amide is filtered and washed with water. Yield 5.5 g with m. pt. 206-207°. After two crystallizations from alcohol the amide of 6-nitro-ac-tetrahydro-2-naphthoic acid melts at 209-210°. Colorless crystals, poorly soluble in cold alcohol and acetone, readily soluble in the same solvents when heated.

6.520 mg substance: 0.745 ml N_2 (21.0°, 726.5 mm). Found %: N 12.68 $C_{11}H_{12}O_3N_2$. Calculated %: N 12.73.

6-Amino-ac-tetrahydro-2-naphthoic acid. A solution of 4.4 g 6-nitro-ac-tetrahydro-2-naphthoic acid in 150 ml ethyl alcohol (temperature about 40°) is agitated in a hydrogen atmosphere in presence of 5 g Ni catalyst (Raney). At the end of the reduction (1350 ml hydrogen absorbed) the catalyst is filtered off, and the alcohol distilled off in vacuum. To the residue is added a small amount of water which precipitates colorless needles of the amino acid. During the melting point determination the substance begins to soften at about 70° and finally melts at 140-145°. This behavior is apparently due to the presence of water of crystallization. The amino acid is heated in a porcelain beaker at 130-140° until no more water vapor comes off. The cooled solid melt is pulverized and recrystallized from toluene to give 3.3 g 6-amino-ac-tetrahydro-2-naphthoic acid with m. pt. 144-145°. The compound is readily soluble in methyl and ethyl alcohols and acetone, and, on heating, in water and toluene.

6.407 mg substance: 3.37 ml 0.01 N H_2SO_4. Found %: N 7.36. $C_{11}H_{13}O_2N$. Calculated %: N 7.33.

Decarboxylation of 6-amino-ac-tetrahydro-2-naphthoic acid. 1.5 g of the amino acid is triturated with 4 g

$Ba(OH)_2$ and a very small quantity of methyl alcohol. The carefully dried mixture is dry-distilled at the ordinary pressure. The distillate (a solid) is extracted with ether, the ethereal solution is washed with alkali solution and dried with potassium hydroxide. The residue after distillation of the ether is a yellow substance with m. pt. 90-95°. After recrystallization from petroleum ether it melts at 107-109° (light-orange leaflets). This melting point is close to that of 2-naphthylamine. A mixed sample with 2-naphthylamine melts at 109-111° (pure 2-naphthylamine has m. pt. 110-112°).

6-Acetamino-ac-tetrahydro-2-naphthoic acid. A small amount of 6-amino-ac-tetrahydro-2-naphthoic acid is acetylated with acetic anhydride under gentle heating (50°) for 30 minutes. The reaction mixture is extracted with boiling water. Needlets of the acetyl derivative come down after cooling. 6-Acetamino-ac-tetrahydro-2-naphthoic acid recrystallizes from water as colorless needles with m. pt. 206-207°, readily soluble in alcohol and in hot water.

5.665 mg substance: 0.318 ml N_2 (21.0°, 726.5 mm). Found %: N 6.23. $C_{13}H_{15}O_3N$. Calculated %: N 6.01.

6-Nitro-ac-tetrahydro-2-naphthylamine (hydrochloride). 5.5 g 6-nitro-ac-tetrahydro-2-naphthoic acid amide is dissolved with heating in 50 ml dry methyl alcohol. The hot solution of the amide is poured into a sodium methylate solution prepared from 1.15 g Na and 25 ml dry methyl alcohol. To the mixture is gradually added 4.0 g Br_2. The reaction temperature is held at 40-50° for 10 minutes, and then acetic acid is added until neutral to litmus. The alcohol is removed by heating on the water bath and the residue treated with water to remove mineral salts. There is obtained 5.8 g substance with m. pt. 135-175°, consisting of a mixture of urethane and unreacted amide.

2.8 g of the product with m. pt. 135-175° is saponified by heating with 12 ml strong hydrochloric acid at 130-140° for 4 hours in a sealed tube. The contents of the tube (crystalline precipitate) are filtered off and the precipitate treated with boiling water. The hot solution is quickly filtered. The water-insoluble substance is 6-nitro-ac-tetrahydro-2-naphthoic acid with m. pt. 195-198° (0.8 g). To the aqueous filtrate is added a large amount of concentrated hydrochloric acid. After a short time light-yellow needlets of 6-nitro-ac-tetrahydro-2-naphthylamine hydrochloride come down (1.1 g). Evaporation of the hydrochloric acid mother liquor yields a further 0.3 g. The hydrochloride crystallizes nicely from ordinary alcohol (it is insoluble in absolute alcohol). It chars when heated in a capillary to 230° (does not melt).

7.000 mg substance: 0.752 ml N_2 (20.0°, 721.0 mm). Found %: N 11.87. $C_{10}H_{12}O_2N_2 \cdot HCl$. Calculated %: N 12.24.

Acetyl-(6-nitro-ac-tetrahydro-2-naphthylamine). A mixture of 0.9 g 6-nitro-ac-tetrahydro-2-naphthylamine hydrochloride, 5 ml benzene, 1.5 ml acetic anhydride and 1 g dry potassium acetate is heated for 30 minutes. On cooling, the precipitate is filtered off and washed with benzene and water. Recrystallization from aqueous alcohol gives 0.4 g of substance with m. pt. 173-175°. From the benzene solution separates an additional 0.3 g with m. pt. 170-171° (after recrystallization from aqueous alcohol). Both lots are combined and recrystallized from ethyl acetate, giving 0.35 g acetyl-(6-nitro-ac-tetrahydro-2-naphthylamine) with m. pt. 176-177°, in the form of fine leaflets with a light-yellow color, readily soluble in acetone, alcohol, and, on heating, water and ethyl acetate. The mother liquor yields a further 0.2 g with m. pt. 170-171°.

3.967 mg substance: 3.30 ml 0.01 N H_2SO_4. Found %: N 11.65. $C_{12}H_{14}O_3N_2$. Calculated %: N 11.96.

Diacetyl-(2,6-tetrahydronaphthylenediamine). 0.35 g acetyl-(6-nitro-ac-tetrahydro-2-naphthylamine) is dissolved in 20 ml absolute ethyl alcohol. To the solution is added 4 g Raney Ni catalyst and the mixture shaken in a hydrogen atmosphere until absorption of the required amount of hydrogen (100 ml). At the end of the reduction the catalyst is filtered off and the alcohol distilled off in vacuum. The residue is triturated with 0.6 ml acetic anhydride and 2 ml absolute benzene. A white crystalline precipitate is formed with m. pt. 239°; recrystallized from aqueous alcohol, the m. pt. is 240.5-241°, corresponding to the m.p. of diacetyl-(2,6-tetrahydronaphthylenediamine).*

4.708 mg substance: 3.80 ml 0.01 N H_2SO_4. Found %: N 11.30. $C_{16}H_{18}O_2N_2$. Calculated %: N 11.38.

SUMMARY

Nitration of ac-β-tetrahydronaphthoic acid gives 6-nitro-(1,2,3,4)tetrahydro-2-naphthoic acid; its structure was established and preparations were effected of its simplest derivatives and of the corresponding 6-amino-(1,2,3,4)-tetrahydro-2-naphthoic acid.

LITERATURE CITED

[1]. Windaus, Ber., 57, 1731 (1924).

Received January 13, 1951. S.Ordzhonikidze All-Union Chemical-Pharmaceutical Scientific Research Institute

* Windaus gives 240° for the m.p. of diacetyl-(2,6-tetrahydronaphthylenediamine) [1].

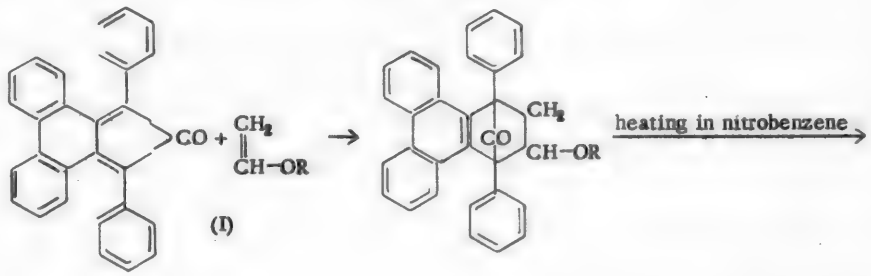
DIENE SYNTHESIS WITH ANISYLCYCLONE AND SOME OTHER CYCLONES

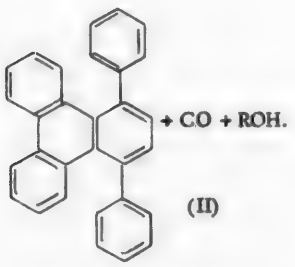
V. S. Abramov and L. A. Shapshinskaya

Phenylated derivatives of cyclopentadienone – cyclones – are extremely reactive substances. They possess a cis-butadienoid system of conjugated double bonds activated by the carbonyl group. Such a system is bound to readily undergo the diene synthesis. This has actually proved to be the case by a series of investigators who reacted cyclones with various dienophiles: maleic anhydride [1], p-quinone, α-naphthoquinone [2], allyl alcohol, allyl chloride [3], phenylated derivatives of ethylene [1] and acetylene, phenylpropiolic aldehyde, phenylpropiolic acid, the methyl ester of acetylenedicarboxylic acid, acetylene [4], etc.

The diene synthesis with cyclones proceeds at moderate temperatures and with relatively brief heating. Particular ease of addition is noted in the case of phencyclone, the reactions with which sometimes proceed at room temperature.

Reactions of cyclones with compounds containing the vinyl radical have previously been investigated by V. S. Abramov [5] who described reactions of vinyl ethers and esters, as well as of vinyl bromide, with acecyclone, cyclone, piperylcyclone, and aceanthrenecyclone. The reactions with vinyl ethers proceed at 180-200°. In the reactions of vinyl ethers with all of the above-listed cyclones the endocarbonyl bridge is ruptured and cleavage occurs of either a molecule of alcohol (in the case of vinyl ethers) or of a molecule of acid (in the case of esters) to yield the corresponding hydrocarbons. A similar course is followed with unsaturated compounds of the type of vinyl bromide. Phencyclone (I) adds on both vinyl ethers and esters with considerably greater ease than other cyclones. Unlike other cyclones, phencyclone reacts with vinyl ethers and vinyl bromide to give addition products in which the endocarbonyl bridge is retained in accordance with the scheme [8]:





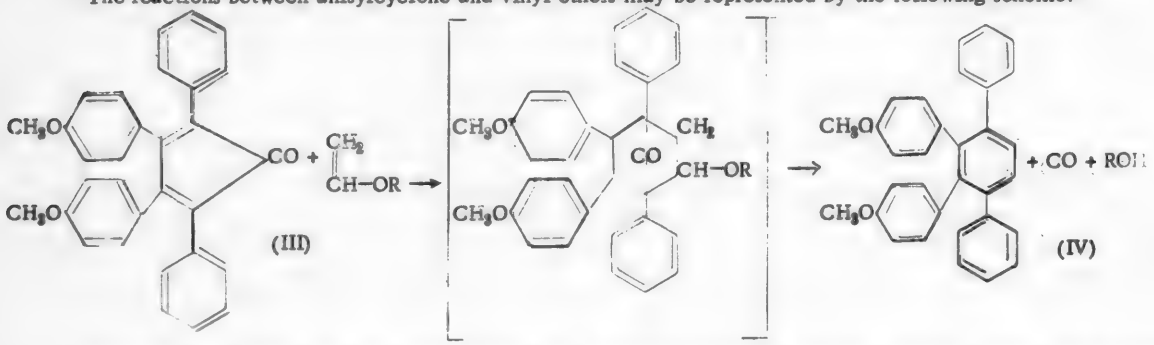
When the products of addition of vinyl compounds to phencyclone are heated in high-boiling solvents such as tetrahydronaphthalene and nitrobenzene, the endocarbonyl bridge is broken and cleavage occurs of a molecule of alcohol or acid to give a hydrocarbon (II).

The purpose of the present investigation was the study of the behavior of anisylcyclone (III) in diene syntheses with vinyl compounds of the type of $CH_2=CHX$ where X is any noncarbon atom.

Diene syntheses of anisylcyclone with vinyl ethers and esters were performed in sealed tubes in a medium of benzene. The reaction mass in the tubes was heated to a temperature of 150-160° for 10 to 20 hours.

The investigation has revealed that the diene synthesis of anisylcyclone with vinyl compounds proceeds analogously to that of tetracyclone and other cyclones (except phencyclone), i.e., in the conditions of the diene synthesis the endocarbonyl bridge is broken and cleavage occurs of an alcohol (with ethers), an acid (with esters), or hydrogen bromide (in the case of vinyl bromide).

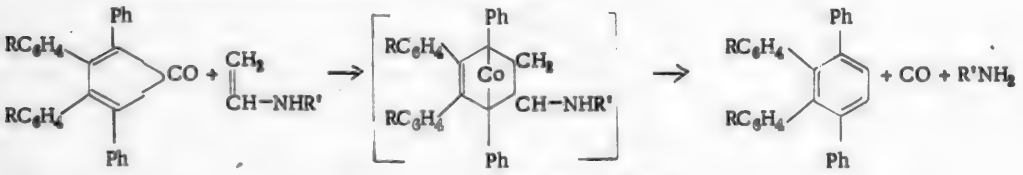
The reactions between anisylcyclone and vinyl ethers may be represented by the following scheme:



Reactions were performed with vinyl n-butyl ether, vinyl isoamyl ether, trivinyl glyceryl ether, vinyl phenyl ether, vinyl acetate and vinyl bromide. All these reactions give one and the same product: 1,4-diphenyl-2,3-di-(p-methoxyphenyl)-benzene (IV). The identity of the 1,4-diphenyl-2,3-di-(p-methoxyphenyl) benzene obtained in the various diene syntheses was established by mixed melting point determinations, when no depression was observed. The hydrocarbon forms white, well-defined, lustrous crystals with m. pt. 180-181°.

In addition we studied the action of vinylamino compounds containing a tertiary nitrogen atom on cyclone and anisylcyclone as representatives of dienes. Vinylamino derivatives (N-vinylethanolamine and N-vinylcaprolactam) were selected because an amino group has an effect on electron displacement contrary to that of other vinyl compounds (vinyl ethers). We therefore hoped to obtain products of addition to cyclones. Contrary to our expectations the N-vinyl derivatives react with cyclones in accordance with the usual scheme, i.e., with cleavage of the endocarbonyl bridge and detachment of the corresponding amine or of caprolactam. This behavior of vinylamino derivatives may probably be explained by the influence of the other groups in their molecules. Owing to lack of experimental material we are unable to draw a definite conclusion.

The reaction proceeds according to the scheme:



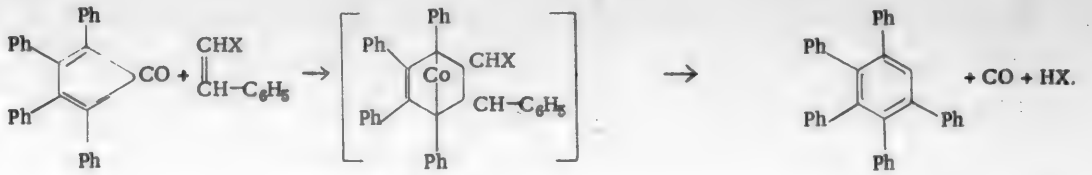
where R = H or OCH_3, and R' = $-CH_2-CH_2OH$ or $CH_2-CH_2-CH_2$ / $CO-CH_2-CH_2$

The reactions were performed in sealed tubes in a benzene medium and at temperatures of 170-200°. The hydrocarbon, 1,2,3,4-tetraphenylbenzene is easily isolated in the pure state when starting from tetracyclone; the same applies to 1,4-diphenyl-2,3-di-(p-methoxyphenyl) benzene when starting from anisylcyclone. These hydrocarbons were identified with the help of the mixed melting point determinations with products isolated from other similar diene syntheses.

It was not possible to isolate in the pure state the detached ethanolamine and caprolactam because small amounts were used in the experiments and they resinified in the experimental conditions.

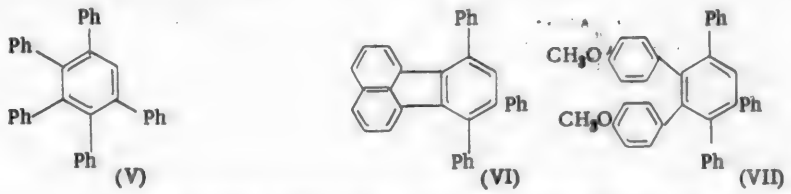
We also investigated the diene synthesis of cyclones with ω-bromostyrene and ω-nitrostyrene.

It was to be expected that the reactions would proceed by the usual mechanism with rupture of the endocarbonyl bridge and cleavage of hydrogen bromide (in the case of ω-bromostyrene) and of nitrous acid (in the case of ω-nitrostyrene):



where X = Br or NO_2.

The reaction of tetracyclone and ω-nitrostyrene has been described in the literature [8]; we have repeated it and extended it to acecyclone and anisylcyclone. The reactions of ω-bromostyrene with cyclone, acecyclone and anisylcyclone were also studied. The reactions were conducted under roughly the same conditions as described above. In all cases hydrocarbons were isolated which we identified through the mixed melting point determinations. The following were obtained: Pentaphenylbenzene (V) in reactions with cyclone; 1,4,5-triphenyl-2,3-(1,8-naphthylene) benzene (VI) in reactions with acecyclone; and 1,4,5-triphenyl-2,3-di-(p-methoxyphenyl) benzene (VII) in reactions with anisylcyclone.



The presence of hydrogen bromide and oxides of nitrogen was detected qualitatively when the tubes were opened.

The experiments entitle us to regard the described reactions as general reactions for cylcones taking place according to the usual scheme of the diene synthesis with vinyl compounds.

We extend our sincere thanks to Corresponding Member of the Academy of Sciences of the U.S.S.R., B. A. Arbuzov for his interest in our work and his general guidance.

EXPERIMENTAL

Action of vinyl n-butyl ether on anisylcyclone [7]. 0.5 g anisylcylcone, 2 ml vinyl n-butyl ether (b. pt. 93.8°) and 15 ml dry benzene were heated in a sealed tube at 150-160° for 14 hours. The reaction was considered at an end when the contents of the tube were decolorized The tube was then opened, the benzene distilled off, and alcohol added to the residue when a light-pink, finely crystalline precipitate came down. This was filtered off and washed several times on the filter with ether. After recrystallization from acetone the product melted at 180-181°. Yield 0.4g or 80% of theory.

0.1284 g substance: 0.4070 g CO_2; 0.0684 g H_2O. Found %: C 86.45; H 5.96. $C_{28}H_{26}O_2$. Calculated %: C 86.88; H 5.88.

Action of vinyl isoamyl ether on anisylcyclone. 0.5 g anisylcyclone, 2 ml vinyl isoamyl ether (b. pt. 105-110°) and 15 ml dry benzene were heated in a sealed tube at 150-160° for 23 hours until the contents had decolorized. The tube was opened, the benzene distilled off. On standing, the residue deposited fine, pink crystals. Recrystallization from acetone gave stout, lustrous, colorless crystals which melted at 180-181°. Yield 0.37 g or 73% of theory. A mixed sample with the above-described product melted at 180-181°.

The substance prepared was 1,4-diphenyl-2,3-di-(p-methoxyphenyl) benzene.

Action of vinyl phenyl ether on anisylcyclone. 0.5 g anisylcyclone, 2 ml vinyl phenyl ether (b. pt. 153-154°) and 15 ml dry benzene were heated in a sealed tube at 147° for 70 hours until the contents decolorized. The tube was opened and the benzene distilled off from the reaction products. From the residue was obtained a crystalline product which after recrystallization from acetone melted at 180-181°. Yield 0.33 g or 65% of theory. A mixture with the above-described preparations of 1,4-diphenyl-2,3-di-(p-methoxyphenyl) benzene melted at 180-181°.

Action of trivinyl glyceryl ether on anisylcyclone. 0.5 g anisylcyclone, 2 ml trivinyl glyceryl ether and 15ml dry benzene were heated in a sealed tube at 110-120° for 20 hours and at 140-150° for 20 hours until the red color of anisylcyclone had disappeared. The tube was opened and the benzene distilled off. To the residue was added alcohol and immediately a fine, pale-pink powder came down. It was filtered and recrystallized from

acetone. M. pt. 180-181°. Yield 0.3 g or 60% of theory. In admixture with 1,4-diphenyl-2,3-di-(p-methoxyphenyl) benzene it melted at 180-181°.

Action of vinyl acetate on anisylcyclone. 0.5 g anisylcyclone, 1.5 ml vinyl acetate (b. pt. 72-73°) and 15 ml dry benzene were heated in a sealed tube at 155-165° for 30 hours. The tube was opened and the benzene distilled off. The solidified residue was recrystallized from alcohol and then from acetone. M. pt. 180-181°. Yield 0.38 g or 76% of theory.

A mixed specimen with other products of similar reactions (1,4-diphenyl-2,3-di-(p-methoxyphenyl)-benzene melted at 180-181°.

Action of vinyl bromide on anisylcyclone. 0.5 g anisylcyclone, 1 ml vinyl bromide and 15 ml dry benzene were heated in a sealed tube at 120° for 10 hours and at 150° for 10 hours. The contents of the tube partly resinified. When the tube was opened it was noticed that pressure had developed and gaseous hydrogen bromide came off. The benzene was distilled off. The residue was diluted with ether and a dark precipitate came down which was filtered off and recrystallized from acetone. The product did not contain halogen when tested by burning on copper oxide. After three recrystallizations from acetone the melting point was constant at 180-181°. Yield 0.25 g or 50% of theory. A mixed sample with the products of reaction of anisylcyclone with vinyl ethers melted at 180-181°.

Action of N-vinylethanolamine on cyclone. 0.4 g cyclone, 0.3 g N-vinylethanolamine and 15 ml dry benzene were heated in a sealed tube under carbon dioxide in a boiling water bath for 10 hours, and the reaction was then completed by heating at 168° for 8 hours. The contents of the tube were poured into a crystallizing dish, and following removal of the greater part of the benzene there separated brown crystals badly contaminated with resin. The resin was washed out with ether. The reaction product was dissolved in a mixture of alcohol and benzene and digested with animal charcoal. Cooling of the filtrate was followed by separation of well-formed, lustrous-white crystals, with m. pt. 189-190°. Yield of pure product 0.15 g or 37.4% of theory. The Lassaigne test for nitrogen gave a negative result. A mixed sample with 1,2,3,4-tetraphenylbenzene melted at 190-191°.

Action of N-vinylcaprolactam on cyclone. 0.4 g cyclone, 0.2 g N-vinylcaprolactam and 15 ml dry benzene were heated in a sealed tube under carbon dioxide at 160-180° for 8 hours and the reaction then completed by heating at 200° for 8 hours. The reaction products were transferred to a crystallizing dish and the benzene evaporated at room temperature, leaving a crystalline mass saturated with resin. The latter was washed out with ether. The crystalline residue was recrystallized from a mixture of alcohol and benzene. M. pt. 189-190°. Yield 0.2 g or 50% of theory. A mixed sample with 1,2,3,4-tetraphenylbenzene melted at 190°.

Action of N-vinylethanolamine on anisylcyclone. 0.4 g anisylcyclone, 0.3 g N-vinylethanolamine and 15 ml dry benzene were heated in a sealed tube under carbon dioxide at 170° for 10 hours. The contents were poured into a crystallizing dish and the benzene evaporated. The residue of dark-brown resin dissolved readily in ether. At the bottom of the dish remained a fine, dark powder. Careful washing with ether and recrystallization from alcohol-acetone and then from acetone gave crystals with m. pt. 180-181°. The Lassaigne test for nitrogen gave a negative result. Yield of pure product 0.1 g or 25% of theory. A mixed sample with the product of reaction of anisylcyclone with vinyl ethers melted at 180-181°.

Action of N-vinylcaprolactam on anisylcyclone. 0.4 g anisylcyclone, 0.2 g N-vinylcaprolactam and 15 ml dry benzene were heated in a sealed tube at 160° for 10 hours and then at 180° for 10 hours. A crystalline residue contaminated with resin was obtained after removing the benzene. The resin was washed out with ether. The crystalline residue was recrystallized from acetone-alcohol and then from acetone. Lustrous crystals with m. pt. 180-181°. Nitrogen was absent. Yield of pure product 0.3 g or 75% of theory. A mixed specimen with the above-described product melted at 180-181°.

Action of ω-nitrostyrene on cyclone [7]. 0.5 g cyclone, 0.3 g ω-nitrostyrene and 10 ml dry benzene were heated in a sealed tube at 170° for 30 hours until the color had disappeared. The solvent was distilled off and to the residual light-yellow oil was added ether to bring down white crystals which after recrystallization from alcohol melted at 244-245°. Yield 0.3 g or 50.8% of theory. The product did not contain nitrogen. No depression in melting point when mixed with pentaphenylbenzene.

Action of ω-nitrostyrene on acecyclone. 1 g acecyclone, 0.6 g ω-nitrostyrene and 15 ml dry benzene were heated in a sealed tube at 170° for 30 hours. The benzene was distilled off. The residual resin was diluted with ether when the resinous portion dissolved to leave a residue of yellow powder. The latter was filtered, well-washed with ether and recrystallized from a mixture of equal parts of alcohol and benzene and then from petrol M. pt. 194-195°. Yield 0.77 g or 68.7 % of theory. No depression of melting point in admixture with the product of reaction of bromostyrene and acecyclone.

Action of ω-nitrostyrene on anisylcyclone. 0.5 g anisylcyclone, 0.3 g ω-nitrostyrene and 15 ml dry benzene were heated in a sealed tube at 160° for 10 hours and then at 180° for 10 hours. Pressure was released when the tube was opened and the odor of oxides of nitrogen was noticed. After removal of the benzene the residual crystalline product was well-washed with ether and recrystallized from a mixture of alcohol and acetone to give stout white crystals with m. pt. 222-223°. Nitrogen was absent. Yield of pure product 0.4 g or 70% of theory.

0.0914 g substance: 0.2926 g CO_2; 0.0486 g H_2O. Found %: C 87.31; H 5.91. $C_{28}H_{24}O_2$. Calculated %: C 88.03; H 5.79

Action of ω-bromostyrene on cyclone. 0.5 g cyclone, 1 ml ω-bromostyrene and 15 ml dry benzene were heated in a sealed tube at 150-160° for 12 hours and at 180-190° for 15 hours until the color had disappeared. On opening the tube a large amount of hydrogen bromide came off. The benzene was distilled off to a third of its volume and alcohol was added to the residue. The product crystallized and was filtered off and recrystallized twice from a mixture of equal parts of methyl alcohol and benzene. M. pt. 244-245°. Yield 0.45 g or 83.3% of theory. The melting point was not depressed in admixture with pentaphenylbenzene.

Action of ω-bromostyrene on acecyclone. 1 g acecyclone, 1.5 ml ω-bromostyrene and 15 ml dry benzene were heated in a sealed tube at 150-160° for 12 hours and at 180-190° for 15 hours. A large amount of hydrogen bromide came off when the tube was opened. The solvent was distilled off and ether added to the residue; crystals came down at once. These were filtered and twice recrystallized from a mixture of equal parts of methyl alcohol and benzene. M. pt. 194-195°. Yield 0.8 g or 66.6% of theory.

0.1016 g substance: 0.3520 g CO_2; 0.0504 g H_2O. Found %: C 94.47; H 5.56. $C_{30}H_{22}$. Calculated %: C 94.88; H 5.22.

Action of ω-bromostyrene on anisylcyclone. 0.3 g anisylcyclone, 0.4 g ω-bromostyrene and 15 ml dry benzene were heated in a sealed tube under carbon dioxide at 150-160° for 15 hours and at 180-190° for 10 hours. A small amount of hydrogen bromide came off when the tube was opened. The solvent was distilled off and ether added to the resinous residue. The resin dissolved and crystals remained at the bottom of the crystallizing dish. These were twice recrystallized from alcohol-acetone. M. pt. 222-223°. Yield of pure product 0.2 g or 66.66% of theory. Halogen was found to be absent in the copper oxide test.

A sample mixed with the product of reaction of anisylcyclone with ω-nitrostyrene melted at 222-223° and did not show any depression.

SUMMARY

1. Anisylcyclone reacts with vinyl ethers and esters and with vinyl bromide according to the diene synthesis reaction.

2. During the diene synthesis the endocarbonyl bridge is ruptured and cleavage occurs of alcohol (in the case of vinyl ethers) and of acid (in the case of vinyl esters), or of hydrogen bromide (in the case of vinyl bromide); all these reactions yield one and the same product – 1,4-diphenyl-2,3-di-(p-methoxyphenyl)benzene (VIII).

3. Tetracyclone and anisylcyclone react with N-vinyl derivatives (N-vinylethanolamine and N-vinylcaprolactam) according to the usual synthesis with vinyl compounds with rupture of the endocarbonyl bridge and cleavage of amine or caprolactam.

4. Tetracyclone, acecyclone and anisylcyclone react with ω-bromostyrene and ω-nitrostyrene according to the usual scheme with rupture of the endocarbonyl bridge and cleavage of hydrogen bromide or the elements of nitrous acid.

LITERATURE CITED

[1] W. Dilthey, O. Trosken, Ber., 66, 1627 (1933); 67, 1958 (1934); W. Dilthey, A. Schaefer, J. prak. Chem., 148, 53 (1937). [2] B. A. Arbuzov, V. S. Abramova and Ya. Devyatov, J. Gen. Chem., 9, 1559 (1939); W. Dilthey, Ber., 73, 430 (1940). [3] V. S. Abramov and Mitropolitanskaya, J. Gen. Chem., 10, 205 (1940); V. S. Abramov and N. P. Tsyplenkova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1944, 60. [4] W. Dilthey, Ber., 71, 974 (1938); W. Dilthey and S. Henkels, J. prak. Chem., 149, 35 (1937); W. Dilthey and Hurtig, Ber., 67, 2004 (1934). [5] V. S. Abramov, Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci., 1945, 330. [6] V. S. Abramov, Proc. Acad. Sci., U.S.S.R., 62, 5 (1948). [7] W. Dilthey, O. Trosken, K. Pium, J. prak. Chem., 141, 331 (1934). [8] Allen and Bell, J. Org. Chem., 8, 3736 (1943).

Received January 20, 1951

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INVESTIGATION OF THE ALKALOIDS OF MAKROTOMIA ECHIOIDES

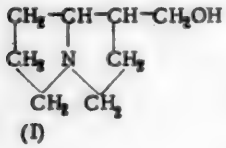
I. A NEW ALKALOID, MACROTOMINE, AND ITS STRUCTURE

G. P. Menshikov and M. F. Petrova

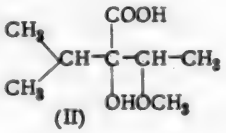
The habitat of Makrotomia echioides, a plant belonging to the borage family (Borraginaceae), is the Transcaucasus. Alkaloids were first detected in it by P. S. Massagetov who also collected specimens for this investigation.

Applying the usual method of dichloroethane extraction of the dry above-ground parts of the plant which had been treated with ammonia, we isolated an alkaloid which crystallized from acetone in the form of large colorless prisms, melting at 95-97°. This alkaloid is a saturated substance with the composition $C_{15}H_{27}O_5N$ and $[\alpha]_D^{}-6.9°$. Judging by these data and also by its other properties, the alkaloid is a new and previously undescribed substance, and we have therefore given it the name of "macrotomine". The content of the latter in the air-dry above-ground parts of the plant does not exceed 0.4%. Alkaline hydrolysis of macrotomine yielded only an amino alcohol with the composition $C_8H_{15}ON$ and acetone (the latter identified through the semicarbazone). A direct comparison showed the amino alcohol to be identical with trachelantamidine, previously obtained by us by hydrolysis of other alkaloids of plants of the borage family [1] and whose structure had been established by one of us (I) [2]. This result of hydrolysis showed that macrotomin is an ester of the already known trachelantamidine and an unknown acid which breaks down on hydrolysis. From a comparison of the empirical formulas of macrotomine ($C_{15}H_{27}O_5N$) and trachelant amidine ($C_8H_{15}ON$), it is easily seen that the unknown acid must have the composition $C_7H_{14}O_5$. Three acids are already known, however, out of those obtained by hydrolysis of plant alkaloids from the borage family – heliotrinic [3], trachelantic [4] and viridifloric [5], the basic skeleton of which also contains 7 carbon atoms. The structural formula (II) was established by one of us for heliotrinic acid, and structural formula (III) for viridifloric acid. These formulas show that heliotrinic acid only differs from trachelantic acid in containing a methoxyl in place of a hydroxyl group, while viridofloric acid has precisely the same structure as trachelantic acid of which it is a diastereomer. On the basis of this similarity in structure it is extremely probable that the unknown acid of macrotomine has a similar structure and only differs from trachelantic acid in containing another hydroxyl group which is located at the carbon atom linked to the two methyl groups, as evidenced by the formation of acetone on hydrolysis. In short, we can assume that the acid of macrotomine has the structure of 2-methyl-2,3,4-trihydroxypentane-3-carboxylic acid (IV). For confirmation of our assumption we selected the method of oxidation of the alkaloid with iodic acid. If the acid really has structure (IV), then macromotine itself must have structure (V), and oxidation with iodic acid should therefore proceed with consumption of two atoms of oxygen and formation of acetone, the acid oxalate of trachelantamidine (VI) and acetaldehyde [see structure (V); the broken line shows the place of rupture]. Finally, all this could only occur if trachelantamidine itself did not enter into reaction with iodic acid. In order to test this last point, we performed an experiment in which the oxidation of trachelantamidine with iodic acid was attempted. It was found that the iodic acid was not reduced at all. Furthermore, a similar experiment was performed with macrotomine itself, and it was found that the amount of iodic acid required for oxidation (as determined by titration) was almost precisely two moles per mole of macrotomine, corresponding to one mole of oxygen per mole of alkaloid. These data, which confirmed our above assumption about the structure of macrotomine, prompted us to institute experiments on the oxidation of relatively large amounts of macrotomin for the purpose of a detailed investigation of the resultant products. At first we carried out the oxidation of macrotomine in a strongly acid medium in presence of free sulfuric acid. By this means we isolated and identified the acetone and acetaldehyde anticipated on the basis of formula (V). Concerning the anticipated acid oxalate of trachelantamidine, we isolated in its place the products of its saponification, i.e., trachelantamidine and oxalic acid. It can easily be seen that these results do not conflict with the above postulates and that they form equally convincing evidence of the correctness of our claim that macrotomine has the structure (V). Apart from that, they show that the acid oxalate of trachelantamidine is apparently an extremely unstable substance readily susceptible to

saponification. Assuming that the saponification of this ester proceeded because of the presence of free sulfuric acid in the solution, we carried out experiments on the oxidation of macrotomine with sodium iodate, but even by this method it was impossible to isolate the oxalate of trachelantamidin in the pure form. However, immediately after the oxidation the solution contained a considerable amount of free oxalic acid which could be isolated in the form of the calcium salt. But in addition the solution contained, apparently, the ester as evidenced by the formation of a fresh fairly large quantity of free oxalic acid after saponification of a solution from which all of the free oxalic acid had previously been precipitated in the form of the calcium salt. All this points to the great instability of the acid oxalate of trachelantamidin e which, of course, greatly complicates its separation in the pure form.



(I)



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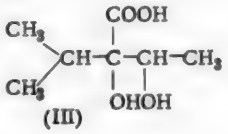

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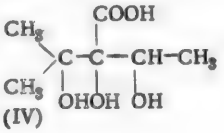
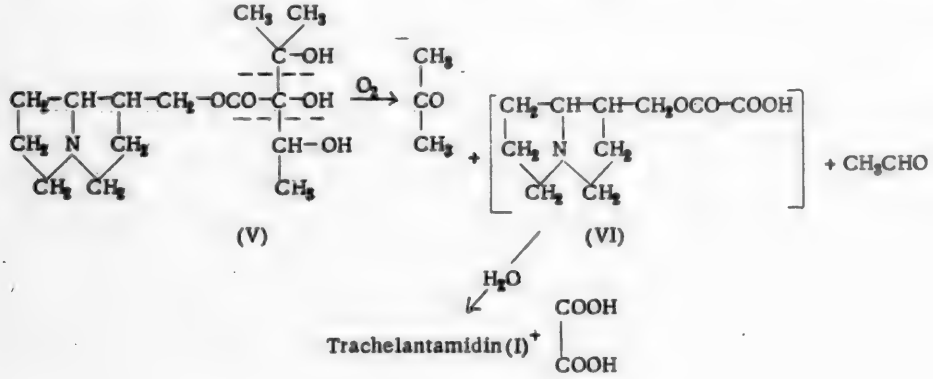


(IV)



(V) (VI)

Trachelantamidin (I)$^+$

EXPERIMENTAL

Isolation and purification of macrotomine. 5 kg pulverized, air-dry, above-ground parts of the plant were processed with 10% ammonia solution until there was a strong odor of ammonia and then exhaustively extracted with dichloroethane (test with silicotungstic acid solution). From the dichloroethane solution the base was extracted with 10% sulfuric acid solution. The acid extract was treated with 20% ammonia solution until strongly alkaline and extracted with chloroform. The chloroform extract was dried with sodium sulfate and filtered before the chloroform was distilled off completely on the water bath. The residual viscous oil crystallized at once when triturated with acetone. The crystalline precipitate was filtered at the pump, washed with a little acetone and recrystallized three times from five times the amount of acetone. After this purification the substance was in the form of large, colorless prisms melting at 95-97° after drying in vacuum (50-55°, 15 mm). The total yield was about 20 g.

0.758 g substance : 10 ml alcohol: l 1 dm; α_D −0.52°, $[\alpha]_D$ −6.9°. 3.830 mg substance: 8.421 mg CO_2; 3.037 mg H_2O. 3.616 mg substance: 7.987 mg CO_2; 2.933 mg H_2O. 7.693 mg substance: 0.325 ml N_2 (25°, 736 mm). 8.766 mg substance: 0.369 ml N_2 (27°, 730 mm). 6.666 ml substance: 1.44 mg CH_4 (17°, 748 mm). Found %: C 59.96, 60.09; H 8.87, 9.07; N 4.67, 460; OH 15.2. $C_{15}H_{27}O_5N$. Calc.%: C 59.76; H 9.03; N 4.64; 3OH 16.94.

Macrotomine is very easily soluble in water and alcohol, less easily soluble in cold acetone and be zene, poorly soluble in ether.

Macrotomine picrate was prepared by mixing alcoholic solutions of the base and picric acid. After crystallization from alcohol the picrate had the form of light-yellow fine needles, melting without decomposition at 130-132°.

5.115 mg substance: 0.465 ml N_2 (22°, 756 mm). Found %: N 10.46. $C_{15}H_{27}O_5N \cdot C_6H_3O_7N_3$. Calculated %: N 10.56.

Saponification of macrotomine. 5 g of the alkaloid was dissolved in 20 ml of 2 N sodium hydroxide,

and the solution heated for 2 hours under a reflux condenser on the boiling water bath. The condenser was then placed in the sloping position and 10 ml was distilled off from the solution at normal pressure. To the distillate were added dry semicarbazide hydrochloride and sodium acetate. A crystalline precipitate at once appeared and was recrystallized from alcohol. It melted at 190° and did not depress the melting point of acetone semicarbazide. The alkaline solution from which the acetone had been distilled off with water was extracted with chloroform. The chloroform extract was dried with sodium sulfate and the chloroform distilled off to leave an oil which was distilled in vacuum (16 mm) at 142°. The distilled base was identified as trachelantamidine both from its properties and from the properties of the salts prepared from it.

The alkaline solution from which the trachelantamidine had been extracted with chloroform was treated with 20 ml 2 N hydrochloric acid solution, and the water was completely distilled off therefrom in vacuum (15 mm). The residue was finally dried by addition of absolute alcohol which was then distilled off, and the dried residue was extracted with hot absolute alcohol. The alcohol solution was filtered from inorganic salts and the solvent distilled off. There remained a viscous oil with an acidic character. All attempts to crystallize it or to prepare crystalline salts from it met with failure. Experiments were also carried out on the saponification of macrotomine with barium hydroxide in which the barium was removed in the form of carbonate, but negative results were likewise obtained. No substances, apart from acetone and trachelantamidine could be isolated in the pure state.

Oxidation of macrotomine with iodic acid in an acid medium To 3 g of the alkaloid were added 40 ml 1 N sulfuric acid solution, 30 ml water and 5 g potassium iodate. The mixture was agitated on a shaking machine until the precipitate had completely dissolved, and the solution was left overnight at room temperature. The next morning the solution was divided into two parts, equal. One of these was placed in a Wurtz flask connected to a wash bottle containing dimedon solution which had been saturated at room temperature. The Wurtz flask was closed with a stopper through which passed a glass tube reaching to the bottom. A stream of air was slowly sucked through for four hours. The crystalline precipitate which separated from the dimedon solution was filtered off. After recrystallization from water it melted at 139-140° and did not depress the melting point of acetaldehyde aldimedon. The solution remaining after distillation of the aceraldehyde in an air stream was repeatedly extracted with ether. After removal of the solvent there remained a crystalline deposit which after recrystallization from water and sublimation was identified as oxalic acid. The solution from which the oxalic acid had been extracted with ether was treated with a large excess of 20% ammonia solution and exhaustively extracted with chloroform. The chloroform extract was dried with sodium sulfate and the chloroform distilled off, leaving an uncrystallizable oil which was identified by direct comparison as trachelantamidine.

The second part of the solution was treated with barium hydroxide until alkaline to phenolphthalein. The solution was freed from the precipitate by decantation and from it was distilled off, at the ordinary pressure, about 15 ml water. The distillate was treated with freshly prepared ammoniacal silver solution for removal of the acetaldehyde. A silver mirror was at once formed. After standing for three hours the precipitate was removed by decantation and from the solution was distilled (using a dephlegmator) 5 ml water at the ordinary pressure. To the distillate was added dry semicarbazide hydrochloride and dry sodium acetate. The resultant precipitate melted at 190° (from alcohol) and did not depress the m.p. of acetone semicarbazone.

Oxidation of macrotomine with sodium iodate. 1.2 g of the alkaloid was dissolved in 30 ml water; to the solution was added 1.9 g sodium iodate, and the whole left for 24 hours at room temperature. To the solution, which had a strong odor of acetaldehyde, was added strong calcium chloride solution. The precipitate was filtered, carefully washed with water, treated with 10 ml of 10% sulfuric acid solution and extracted several times with ether. The ether was driven off from the extract to leave a small amount of crystals identified as oxalic acid.

To the solution from which the free oxalic acid had been precipitated with calcium chloride was added 10 ml 20% sulfuric acid before heating for two hours on the boiling water bath. The hot solution was filtered from inorganic salts, cooled, and repeatedly extracted with ether. After removing the ether, there remained a fairly large amount of crystals, also identified as oxalic acid.

SUMMARY

1. A new crystalline alkaloid, macrotomine, $C_{15}H_{27}O_5N$, was isolated from the Transcaucasian plant Makrotomia echioides, belonging to the borage family. It melts at 95-97° and has m.p. 95-97° and $[\alpha]_D - 6.9°$.

2. Alkaline hydrolysis of macrotomine enables only an amino alcohol of the composition $C_8H_{15}ON$ and acetone to be isolated.

3. The isolated amino alcohol was found to be identical with trachelantamidine, preobtained by hydrolysis of the alkaloids trachelantamine and viridiflorine and for which the structure (I) had already been established.

4. The results of hydrolysis show that macrotomine is an ester of trachelantamidine and an unknown acid which decomposes on hydrolysis to form acetone.

5. Oxidation of macrotomine with iodic acid consumes one mole oxygen per mole alkaloid and yields acetone, trachelantamidine, oxalic acid and acetaldehyde, which points to structure (V) as the only possible one for macrotomine.

LITERATURE CITED

[1] G. P. Menshikov and G. M. Borodina, J. Gen. Chem. 15, 225 (1945); G. P. Menshikov, J. Gen. Chem., 18, 1736 (1948).

[2] G. P. Menshikov, J. Gen. Chem. 16, 1311 (1946).

[3] G. P. Menshikov, J. Gen. Chem. 9, 1851 (1939); Ber. 65, 974 (1932).

[4] G. P. Menshikov, J. Gen. Chem. 17, 343 (1947).

[5] G. P. Menshikov, J. Gen. Chem. 18, 1736 (1948).

Received January 18, 1951 S. Ordzhonikidze All-Union Chemical-Pharmaceutical Research Institute

DELSEMIDINE

IV. INVESTIGATION OF DELPHINIUM ALKALOIDS

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In the investigation of the amorphous mixtures remaining after separation of the crystalline portion of the total alkaloids from Delphinium semibarbatum [1], it was noted that an additional amount of the amino alcohol, delsine, can be obtained by their saponification in alkalies. In the acidic portion of the hydrolysis products, however, was found not delseminic acid (which would have pointed to the presence in the mixture of residues of the alkaloid, delsemine) but methylsuccinylanthranilic acid. A similar observation was made in work with the unseparated portion of the total alkaloids from D. creophilum* [2]. These facts support the belief that the above-mentioned plants possibly contain, in addition to delsemine and delsin; a third base with a structure close to that of delsemine. After some efforts, this alkaloid was actually isolated in the form of the crystalline salt of perchloric acid. The base itself, obtained by decomposition of the perchlorate, was amorphous. Apart from the perchlorate, the crystalline hydroiodide was isolated.

Elementary analysis of the base corresponds to $C_{37}H_{50}O_{10}N_2$. This formula is also confirmed by the summation of the formulas of hydrolytic decomposition of the alkaloid-delsin, $C_{25}H_{41}O_7N$ and methylsuccinylanthranilic acid, $C_{12}H_{13}O_5N$.

On comparing the properties of our alkaloid with the properties of the alkaloids isolated from other varieties of Delphinium, we noted that it closely resembles methyllycaconitine and delartine. The first was found by Goodson [4] in 1943 in Delphinium elatum, the second by Rabinovich and Konovalova [5] in Delphinium sp. (a varietal name not yet established). In the table are compared the physico-chemical constants of the above compounds.

Constants	Delsemidine	Delartine	Methyllycaconitine
Formula of base	$C_{37}H_{50}N_2O_{10}$	$C_{36}H_{52}N_2O_{11}$	$C_{37}H_{48}N_2O_{10}$
Melting point	122-130°•	110-130°	119-128°•
Specific rotation in alcohol	+46.6	+45.1	+49.1
Hydroiodide, dry, melting point	199-202	–	201
" " $[\alpha]$ in 1 N KOH	+18.7	–	+18.5
" " $[\alpha]_D$ 0.2 N KOH	+21.8	–	+24.4
" " $[\alpha]_D$ 0.024 N KOH	–	–	+31.2
" " $[\alpha]_D$ in alcohol	+22.6	–	–
Perchlorate, dry, melting point	194-195	188-190°	–
" " $[\alpha]_D$ in alcohol	+25.4	+25.08	–

According to this table the properties of all three alkaloids are so close that there would hardly appear to be any doubt that they are identical. But when comparing such compounds we must not omit an examination of the products of their saponification. All three bases are esters. Methyllycaconitine hydrolyzes when heated with alkali and forms methylsuccinylanthranilic acid and an amino alcohol which Goodson, from the similarity of some of its

• All the melting points have been corrected for the exposed part of the mercury.

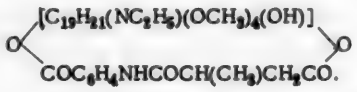
* In 1940 the botanist K. S. Afanasev [3] described a new variety of delphinium — Delphinium rotundifolium — from the northern slopes of the Turkestan mountains. It resembles D. oreophilum but differs from it mainly in its round quinquepartite lower leaves and in the character of its trimming. According to an examination by E. E. Korotkova, director of the botanical group of our institute, the material investigated by us more nearly resembles D. rotundifolium Afan. than D. oreophilum Huth.

properties, took to be lycoctonine. Although the cleavage with formation of methylsuccinylanthranilic acid is also consistent with our own data, there is little probability, as already shown [6], that the amino alcohols lycoctonine and delsin are identical.

On the other hand, although there is hardly any doubt of the identity between delartine and delsine [6], their esterifying acids — delartic and methylsuccinylanthranilic acids — exhibit a series of differing properties. When delartic acid is hydrolyzed in an acid medium it splits up into anthranilic acid and a crystalline substance with m.p. 170-172° whose structure has not yet been elucidated but which apparently contains three carbon atoms. But the acid which we isolated hydrolyzes under analogous conditions to anthranilic and methylsuccinic (m.p. 112°) acids.

On the basis of the above considerations, we propose to call our alkaloid "delsemidine". Whether or not it is identical with methyllycaconitine and delartine will only be decided after a direct comparison of specimens of all three alkaloids.

On the assumption that hydrolysis of delsemidine involves consumption of two equivalents of alkali and that the resultant acid is dibasic, the partially established formula of the alkaloid may be:



EXPERIMENTAL

Isolation of delsemidine. The amorphous mixture remaining after fractionation of the total alkaloids of Delphinium semibarbatum and separation of delsemine is extracted in the cold with small portions of ether. The combined ether extract of the alkaloids is separated into seven fractions by successive extraction with 1 N hydrochloric acid. To each fraction is added a saturated aqueous solution of ammonium perchlorate; from each fraction is at once precipitated a white, soft mass. The acid solutions containing the precipitates are placed in an ice chest. After two days the material in the first three fractions had solidified completely, and fine crystals had appeared on the walls. The crude delsemidine perchlorate was recrystallized from 5 parts of water and 15 parts methanol. The recrystallized salt was pulverized and covered with 10 parts water. Addition was then made of a few milliliters of concentrated ammonia solution. An excess of ammonia was avoided as far as possible. The separated friable precipitate was filtered at the pump, washed a few times with water, and dried in a vacuum desiccator over calcium chloride.

Separation of delsemidine from the total alkaloids of D.oreophilum is effected in a similar manner.

Delsemidine. Free delsemidine, dehydrated by drying in a vacuum at 105°, is a light, amorphous powder with a faint yellow color. It could not be recrystallized from any solvent. The alkaloid is very unstable to alkalies and acids. Even in low-boiling solvents its solutions rapidly darken when heated.

Delsemidine melts in the range 122-130° with frothing. The base is very easily soluble in alcohol, acetone, chloroform and benzene, fairly easily soluble in ether, sparingly soluble in petroleum ether and water.

0.4080 g substance: in 10 ml alcohol; l 10.0; α_D + 1.90°, $[\alpha]_D^{18}$ + 46.6°.

0.1262 g substance: 0.2994 g CO_2; 0.0850 g H_2O. 0.1200 g substance: 0.2850 g CO_2; 0.0808 g H_2O. 0.1042 g substance: 4.10 ml N_2 (23°, 727 mm). 0.1036 g substance: 4.15 ml N_2 (22°, 728 mm). Found %: C 64.74, 64.81; H 7.54, 7.53; N 4.36, 4.44. $C_{37}H_{50}O_{10}N_2$. Calculated %: C 65.08; H 7.38; N 4.10.

Delsemidine hydroiodide. 2.0 g delsemidine is dissolved in 4.0 ml alcohol and the solution acidified with a few drops of 10% hydriodic acid until weakly acid to Congo red. On the following day the contents of the flask are inthe form of a crystalline mass. The salt is drained at the pump and recrystallized from 70% alcohol. Delsemidine hydroiodide crystallizes in the form of very fine needlets containing 3 moles of water of crystallization and usually aggregating to yellow clusters.

0.9284 g substance: 0.0580 g H_2O (105°, in vacuum). Found %: H_2O 6.25. $C_{37}H_{50}O_{10}N_2 \cdot HI \cdot 3H_2O$. Calculated %: H_2O 6.25.

The dehydrated salt melts gradually at 199-202° (with decomposition). It is sparingly soluble in water and alcohol.

Goodson [4] determined the specific rotation of methyllycaconitine hydroiodide in potassium hydroxide solution and reported that $[\alpha]_D$ changes with the concentration of the alkali solution. This behavior was also observed with delsemidine but to a less marked degree.

0.2028 g substance: in 10 ml 0.9675 N alcoholic solution of KOH; l 10.0; α_D + 0.38°, $[\alpha]_D^{27}$ + 18.7°. 0.2017 g substance in 10 ml 0.1935 N alcoholic solution of KOH; l 10.0; α_D + 0.44°, $[\alpha]_D^{29}$ + 21.8°. 0.1994 g substance in 25 ml alcohol; l 10.0; α_D + 0.18°, $[\alpha]_D^{30}$ + 22.6°. 0.1264 g substance: 3.11 ml 0.05 N $AgNO_3$ (potentiometrically). 0.1324 g substance: 3.28 ml 0.05 N $AgNO_3$. Found %: I 15.61, 15.72. $C_{37}H_{50}O_{10}N_2 \cdot HI$ Calculated %: I 15.66.

Delsemidine perchlorate.* After repeated recrystallization from aqueous methanol, the perchlorate is in the form of fine platelets aggregated to large clusters. The salt crystallizes with 1.5 moles water. The dried salt melts at 194-195° with decomposition. Like the hydroiodide, the perchlorate is sparingly soluble in water and alcohol. The solutions have a slight violet fluorescence.

Saponification of delsemidine. Into a solution of 4.0 g delsemidine in 30 ml methanol is poured 11.8 ml of 1.0 N potassium hydroxide (2 equivalents), and the alcohol rapidly distilled off. When the main bulk of the alcohol was evaporated, 10 ml water is added to the residue. After a short time crystallization commences. The crystals are drained, washed with a few milliliters of water and recrystallized from 70% alcohol. The pure crystals have m.p. 139° and do not depress the melting point of delsin. The slightly yellow alkaline mother liquor is exhaustively extracted with ether for removal of traces of delsin, and is then acidified in the cold with 6 ml 1.0 N hydrochloric acid. On the following day the small brown precipitate is filtered off and addition is made to the solution of a further 6 ml of 1.0 N acid. The oil which then separates is left overnight and crystallizes. The filtered and dried crystals melt at 163-164°. A mixed sample with α-methylsuccinylanthranilic acid melts at 164-165°.

The crystals with m.p. 163-164° were recrystallized from hot water. The recrystallized acid melts at 170°. It does not depress the melting point of β-methylsuccinylanthranilic acid. When hydrolyzed in an acid medium, methylsuccinylanthranilic acid splits up into anthranilic and methylsuccinic acids.

SUMMARY

1. An alkaloid, $C_{37}H_{50}O_{10}N_2$, called "delsimidine" has been found in Delphinium semibarbatum and D. oreophilum (D. rotundifolium).

2. When hydrolyzed in alkalies, delsemidine splits up into the amino alcohol, delsin, and the dibasic methylsuccinylanthranilic acid.

3. The possible identity between the alkaloids delsemidine, delartine and methyllycaconitine is discussed.

LITERATURE CITED

[1] S. Yunusov and N. K. Abubakirov, J. Gen. Chem. 21, 199 (1951).**

[2] S. Yunusov and N. K. Abubakirov, J. Gen. Chem. 21, 967 (1951). ***

[3] K. S. Afanasev, Bot. Mat. Herb. Bot. Inst. Acad. Sci. USSR 8, 108 (1940).

[4] J. A. Goodson, J. Chem. Soc. 1943, 139.

[5] M. S. Rabinovich and R. A. Konovalova, J. Gen. Chem. 19, 1387 (1949). ****

[6] S. Yunusov and N. K. Abubakirov, Proc. Acad. Sci. Ukr. SSR, No. 3, 22 (1950).

Received December 2, 1950

Institute of Chemistry of the Academy of Sciences
Uzbek SSR, Tashkent

* 0.6806 g substance: 0.2520 g H_2O (105°, in vacuum). Found %: H_2O 3.70. $C_{37}H_{50}O_{10}N_2 \cdot HClO_4 \cdot 1.5 H_2O$. Calculated %: H_2O 3.34. 0.2364 g substance in 25 ml solution 60% alcohol; l 10.0; α_D + 0.24°, $[\alpha]_D^{29}$ + 25.4°. 0.1466 g substance: 0.0272 g AgCl. 0.1254 g substance: 0.0228 g AgCl. Found %: Cl 4.59, 4.50. $C_{37}H_{50}O_{10}N_2 \cdot HClO_4$. Calculated %: Cl 4.53.

** See Consultants Bureau translation, p. 189.

*** See Consultants Bureau translation, p. 1059.

**** See Consultants Bureau translation, p. 1389.

INVESTIGATION OF THE ALKALOIDS OF TURNEFORCIA SIBIRICA

1. A NEW ALKALOID, TURNEFORCINE

G. P. Menshikov, S. O. Denisova, and P. S. Massagetov

A liquid alkaloid has been isolated from the Transcaucasian plant, Turneforcia sibirica, a member of the borage family. The substance forms well-crystallized salts (picrate, hydrochloride and chloroplatinate). Isolation was effected by the usual method of dichloroethane extraction of the pulverized above-ground parts of the plant after treatment with ammonia solution. The isolated alkaloid, which is present in the plant to the extent of not more than 0.07%, has the composition $C_{13}H_{21}O_3N$; its hydrochloride melts at 169-170° and has $[\alpha]_D^t -58.59°$ (water). Since the alkaloid differs from all previously described bases, we propose the new name of "turneforcine".• Like all the alkaloids which we have isolated from plants of the borage family, it is an ester. Alkaline hydrolysis yielded angelic acid and a saturated amino alcohol of the composition $C_8H_{15}O_2N$ which, following the proposed nomenclature, we give the name of "turneforcidine". Hydrolytic splitting of turneforcine may therefore be represented by the following equation:

$$C_{13}H_{21}O_3N + H_2O = C_8H_{15}O_2N + C_5H_8O_2.$$

Up to now three saturated amino alcohols with the same composition have been known; they were obtained by hydrolysis or other chemical transformations of alkaloids of plants of the Borraginaceae and Compositae families, and have the names platynecine [2], dihydroxyheliotridane [3] and hastanecine [4]. A direct comparison established that turneforcidine was not identical with any of these. Consequently, turneforcine is an ester of angelic acid and the amino alcohol, turneforcidine.

EXPERIMENTAL

Isolation and purification of turneforcine. 6 kg air-dry, pulverized above-ground parts of the plant were moistened with 10% ammonia solution until there was a strong odor of ammonia, and then exhaustively extracted with dichloroethane. The alkaloid was extracted from the dichloroethane solution with sulfuric acid solution. Traces of dichloroethane were removed from the acid solution by extraction with ether, the ether solution was separated, and the acid solution treated with a large excess of 20% ammonia prior to fresh extraction with ether. The ether extract was dried with sodium sulfate and the ether distilled off to leave a residue of uncrystallizable oil. To this was added a cold saturated solution of picric acid in alcohol until acid to methyl orange. A crystalline picrate came down at once and was drained at the pump, washed with alcohol, and recrystallized once from alcohol, giving 7.9 g light-yellow lustrous platelets with m.p. 199.5-201°. The melting point did not change on further recrystallization.

7.415 mg substance: 0.782 ml N_2 (21°, 732 mm). 7.480 mg substance: 0.786 ml N_2 (21°, 732 mm). Found %: N 11.80, 11.76. $C_{13}H_{21}O_3N \cdot C_6H_3O_7N_3$. Calculated %: N 11.96.

The free base was prepared from the picrate by treatment with 10% hydrochloric acid followed by exhaustive extraction of the picric acid with ether. The colorless acid solution was treated with excess of 20% ammonia solution. The alkaloid was extracted with ether, the ether extract dried with sodium sulfate and the ether completely distilled off. From 7 g picrate was obtained 3.4 g of a colorless uncrystallizable oil.

Turneforcine hydrochloride. The alkaloid obtained via the picrate was dissolved in a small amount of absolute alcohol and to the solution was added an alcoholic solution of hydrochloric acid until acid to Congo. Dry ether was then added. On standing at 0° the solution deposited crystals which were reprecipitated with dry ether from absolute alcohol. After reprecipitation the hydrochloride formed colorless needles melting at 169-170°.

0.3619 g substance: 5 ml water; l 0.5 dm; α_D −2.12°; $[\alpha]_D$ −58.59.

• Reference is made in the literature to two alkaloids with the composition $C_{13}H_{21}O_3N$, isolated from Senecio sylvaticus and Senecio Sarracenicus [1], but unfortunately they have been so superficially investigated and so briefly described that it is impossible to decide whether or not they are identical with turneforcine.

3.958 mg substance: 8.188 mg CO_2; 2.788 mg H_2O. 3.403 mg substance: 7.006 mg CO_2; 2.406 mg H_2O. 7.065 mg substance: 0.334 ml N_2 (24°, 740 mm). 0.2815 g substance: 10.12 ml 0.1 N solution $AgNO_3$. Found %: C 56.42, 56.14; H 7.88, 7.91; N 5.28; Cl 12.76, $C_{13}H_{21}O_3N \cdot HCl$. Calculated %: C 56.59; H 8.06; N 5.08; Cl 12.86.

Turneforcine chloroplatinate. To an alcoholic solution of the alkaloid acidified with hydrochloric acid was added 10% platinum chloride solution. On standing the solution deposited crystals which were recrystallized from 1% aqueous hydrochloric acid. Yellow leaflets, m. pt. 154.5-155.5°.

Saponification of turneforcine. 2 g of the alkaloid was treated with 20 ml of 10% sodium hydroxide solution and refluxed on a boiling water bath until dissolved (about 3 hours). The cooled solution was treated with 20% hydrochloric acid solution until acid to Congo and then extracted with ether. The ether extract was dried with sodium sulfate and the ether distilled off, using a dephlegmator. A light-yellow oil remained which at once crystallized when cooled. After recrystallization from water it melted at 43-44° and was identified as angelic acid by direct comparison. The acidic solution from which the angelic acid had been extracted was evaporated and dried in vacuum. The dry residue was extracted with absolute alcohol. The alcoholic solution was filtered and inspissated in vacuum to a volume of 5-6 ml. Addition to this concentrate of sufficient ether to cause turbidity resulted in deposition of crystals (1.2 g) which after reprecipitation from absolute alcohol with dry ether had the form of thin colorless needles with m. pt. 116°.

5.208 mg substance: 3.919 mg AgCl. 6.374 mg substance: 4.768 mg AgCl. Found %: Cl 18.62, 18.51. $C_8H_{15}O_2N \cdot HCl$. Calculated %: Cl 18.32.

The free base was obtained from this hydrochloride by dissolving in a little water, adding a slight excess of dry sodium carbonate to the solution, and completely distilling off the water in vacuum. The residue was dried by distilling off absolute alcohol from it in a vacuum. The dry residue was digested with dry acetone and the hot acetone solution was filtered. Crystals came down on cooling. These were recrystallized twice from 50 times the amount of acetone. The base formed snow-white needles with m. pt. 118.5-120°. A mixture with hastanecine (m. pt. 113-114°) melted at about 85-90°.

0.0528 g substance: 0.791 ml methyl alcohol; l 0.5 dm; α_D −0.35°; $[\alpha]_D$ −10.5°.

5.059 mg substance: 11.264 mg CO_2; 4.225 mg H_2O. 3.564 mg substance: 7.978 mg CO_2; 3.040 mg H_2O. 6.795 mg substance: 0.549 ml N_2 (20°, 730 mm). 6.570 mg substance: 0.534 ml N_2 (20°, 730 mm). Found %: C 60.72, 61.05; H 9.34, 9.54; N 9.04, 9.07. $C_8H_{15}O_2N$. Calculated %: C 61.09; H 9.61; N 8.92.

The base is saturated in character; it does not deoxidize potassium permanganate in 10% sulfuric acid solution.

SUMMARY

1. Isolation was effected from Turneforcia sibirica (Borraginaceae family) of a new, optically active alkaloid with the composition $C_{13}H_{21}O_3N$, named "turneforcine". It was characterized in the form of salts with the following constants: Hydrochloride — m. pt. 169-170°, $[\alpha]_D$ −58.59°; picrate — m. pt. 199.5-201°; chloroplatinate — m. pt. 154.5-155.5°.

2. Alkaline hydrolysis of turneforcine gave angelic acid and a new, hitherto undescribed, saturated amino alcohol with the composition $C_8H_{15}O_2N$, named "turneforcidine".

LITERATURE CITED

[1] A. Muller, Chem. Zentr., 11, 1049 (1925); J. J. Blackie. Chem. Zentr., 1, 2612 (1927).

[2] R. A. Konovalova and A. P. Orekhov, J. Gen. Chem., 8, 273 (1938); Ber., 69, 1908 (1936).

[3] G. P. Menshikov and A. D. Kuzovkov, J. Gen. Chem., 19, 1702 (1949).*

[4] V. S. Konovalov and G. P. Menshikov, J. Gen. Chem., 15, 328 (1945).

Received November 5, 1950 S. Ordzhonikidze All-Union Chemical-Pharmaceutical Research Institute, Moscow

*See Consultants Bureau translation, p. a-137.

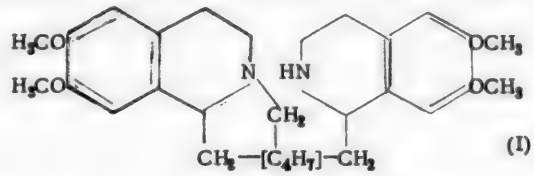
INVESTIGATIONS ON ISOQUINOLINE COMPOUNDS

V. SYNTHESIS OF THE NATURAL ALKALOID, EMETINE*

R. P. Evstigneeva, R. S. Livshits,** M. S. Bainova,

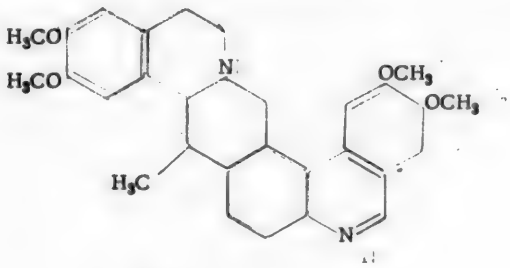
L. I. Zakharkin and N. A. Preobrazhensky

The alkaloid emetine, like morphine, strychnine and curarine, is one of those very important natural compounds whose structure had not hitherto been confirmed by synthesis. It was first prepared in 1817 [1] and in 1879 it was isolated by Podvysotsky [2] in the pure form. As a result of the studies of various transformations of the alkaloid performed by numerous authors over a period of over 100 years [3], it was established that the emetine molecule contains two tetrahydroisoquinoline nuclei linked by a group of seven carbon atoms [4] (I):

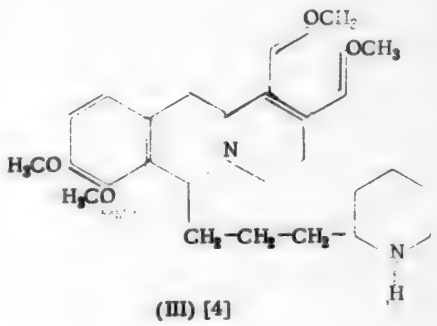


(I)

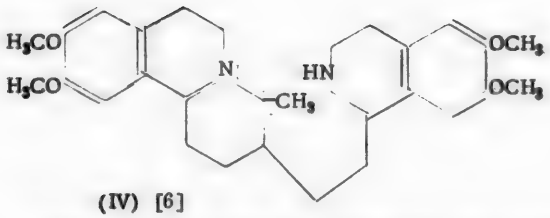
Further elucidation of the structure of emetine proved to be extremely difficult and the following structures were advanced by various authors and then rejected:



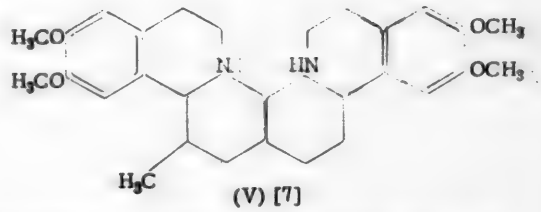
(II) [5]



(III) [4]



(IV) [6]



(V) [7]

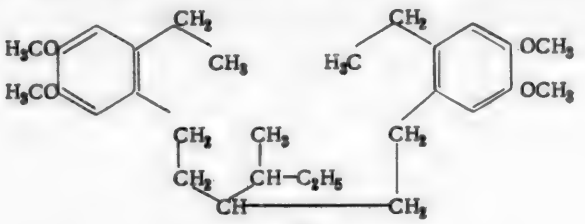
Although the above formulas are consistent with a series of chemical reactions of emetine, not one of them fully reflects the properties of the alkaloid.

In the years 1948-1950 a very large number of papers were published which aimed at clarifying the structure of the central portion of the emetine molecule [8]. In the course of these investigations a systematic study was made

* We described the synthesis of emetine for the first time in Proc. Acad. Sci. U.S S.R., 75, 539 (150). In this paper we present the main experimental data of the investigations.

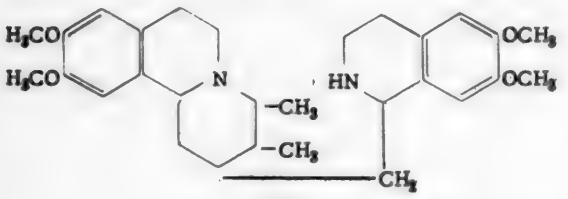
** Deceased.

of the products of destruction of emetine formed mainly by its exhaustive methylation, and a large number of compounds were isolated which were characterized and whose structure was determined. These studies show indisputably that the nonnitrogenous skeleton of emetine has the structure:

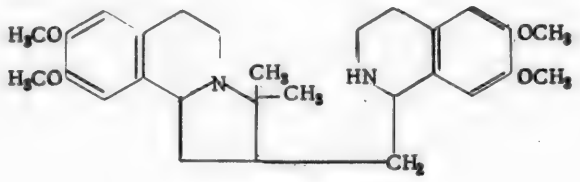


(VI)

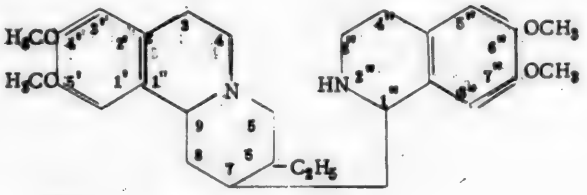
On this basis three possible formulas for the alkaloid can be advanced:



(VII)

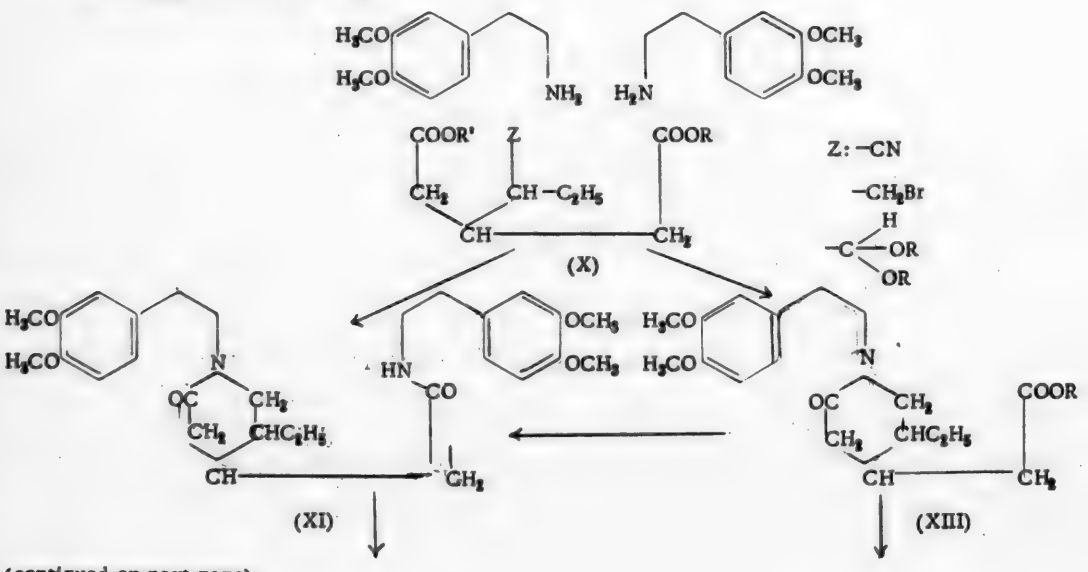


(VIII)



(IX)

Scheme of Emetine Synthesis



(X)

(XI)

(XIII)

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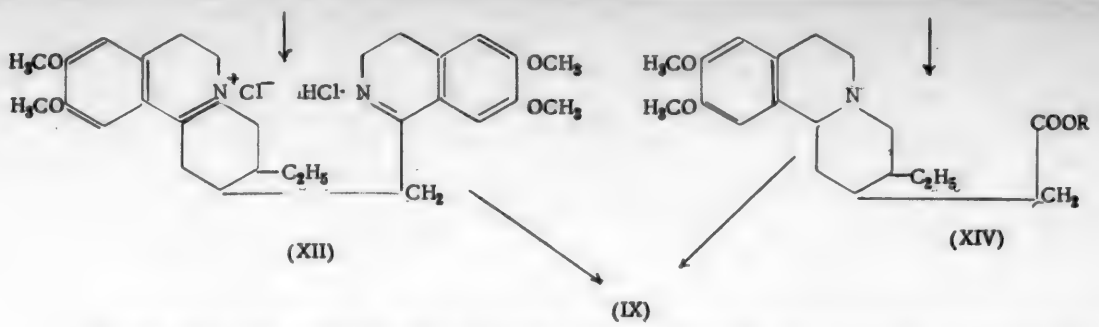


(XII) (XIV) (IX)

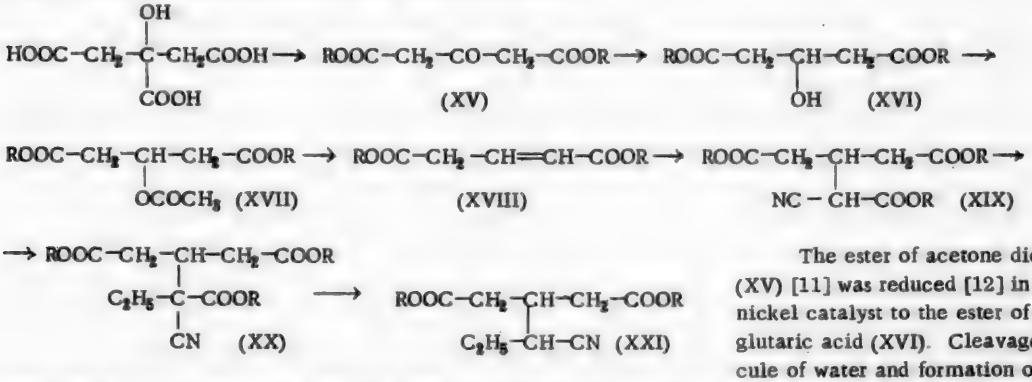
On the basis of our synthetic studies in the field of isoquinoline compounds possessing structures close to those proposed for emetine [9], we arrived at the conclusion that the most probable one was formula (IX). Robinson [10] also reached this conclusion on the basis of his concepts of the structural-genetic relationship of the alkaloids of the isoquinoline group. However, the problem of the structure of emetine could not be considered to be conclusively solved in the absence of a synthesis. This synthesis has now been effected and in this paper we describe our synthesis of emetine.

We had studied several routes to emetine which are characterized by the general scheme set out above.

At the basis of our emetine synthesis lay the idea of utilizing a starting substance in whose structure would previously predominate the whole of the central part of the emetine molecule, i.e., that part most in need of experimental demonstration. The structure of this starting material corresponds to the general formula (X). The presence in the hydrocarbon chain of compound (X) of the requisite and appropriately arranged active groups —(COOH, —CN, $-CH(OR)_2$, $-CH_2Br$, enables to be built up, by condensation with homoveratrylamine, the structure of the quinolizine and isoquinoline systems entering into the structure of emetine.

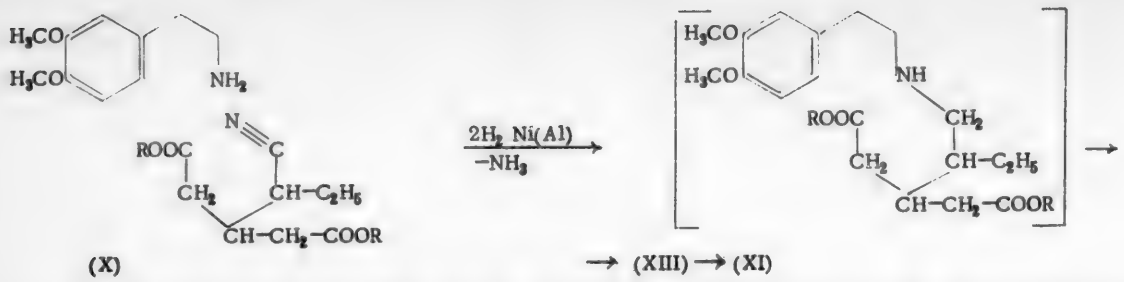
For utilization as starting materials for the central portion of the emetine molecule we synthesized the following compounds: a) the ethyl ester of β-(α'-bromomethoxy)-propylglutaric acid (X) (Z = $-CH_2Br$); b) γ-ethyl-H δ-valerolactone-β-acetic acid; c) the anhydride of β-(α'-diethylacetal)-propylglutaric acid (X) (where Z = $-C(OH)_2$) and d) the ester of β-(α'-cyano)-propylglutaric acid (X) (where Z = —CN).

In this paper we present the synthesis of emetine starting from the ester of β-(α'-cyano)-propylglutaric acid (X), (where Z = —CN), obtained by the following route:



The ester of acetone dicarboxylic acid (XV) [11] was reduced [12] in presence of nickel catalyst to the ester of β-hydroxyglutaric acid (XVI). Cleavage of a molecule of water and formation of the ester of glutaconic acid (XVIII) were effected both by boiling β-hydroxyglutaric acid in benzene and by conversion into the β-acetoxy derivative (XVII) followed by cleavage of a molecule of acetic acid [13]. By condensation with ethylcyanoacetate (XIX) [14] and ethyl iodide in presence of sodium alcoholate there is obtained the ester of β-(α'-cyano-α'-carbethoxy) propylglutaric acid (XX). After saponfication with the calculated amount of sodium alcoholate and water followed by acidification and decarboxylation, there is obtained the ester of β-(α'-cyano)-propylglutaric acid (XXI).

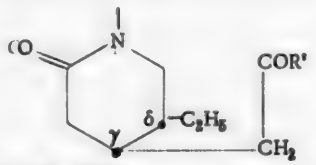
Reductive condensation in presence of nickel or platinum catalyst of the ester of β-(α'-cyano) propylglutaric acid and an excess of homoveratrylamine (route A) leads to addition of the latter to the nitrile group and loss of ammonia [15]. At the same time the resultant secondary amino group enters into reaction with one of the carbalkoxyl groups with formation of an amide bond and closure of the piperidone ring.



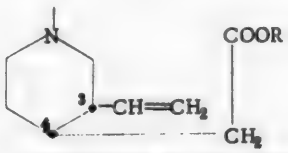
(X) → (XIII) → (XI)

After removal of catalyst and ethyl alcohol, the obtained piperidone derivative (XIII) and excess homoveratrylamine are converted by heating at 180-200° into β"-(3", 4"-dimethoxyphenyl) ethylamide-N-[β'-(3', 4'-dimethoxyphenyl)] ethyl- δ-ethyl-α-piperidone- γ-acetic acid (XI) which comprises a mixture of two stereoisomers: the A-isomer soluble in toluene, and the B-isomer insoluble in toluene.

In this case stereoisomerization similar to that in the quinic alkaloids [16] has taken place, i.e., the presence of A- and B-isomers in compounds (XIII), (XI) and (XII) is the consequence of cis-trans-isomerism at the γ- and δ-carbon atoms:



(XIII), (XI), (XII)



Meroquinene and the corresponding quinine alkaloids

The prepared diamides (XI) are individually subjected to cyclization with phosphorus oxychloride to form the benzquinolizine-isoquinoline derivative (XII). The resultant hydrochlorides of the chloride of 4', 5'-dimethoxy-6-ethyl-7-(1"-methyl-6", 7"-dimethoxy-3", 4"-dihydroisoquinolyl)-3,4,5,6,7,8-hexahydro-9,10-dehydro-(1,2:1', 2')-benzquinolizine (XII) is further hydrogenated in presence of platinum or nickel catalyst, and after appropriate working-up there is obtained 4', 5'-dimethoxy-6-ethyl-7-(1"-methyl-6", 7"-dimethoxy-1", 2", 3", 4"-tetrahydroisoquinolyl)-3,4,5,6,7,8-hexahydro-(1,2:1', 2')-benzquinolizine (IX) – emetine bases.

We also effected a synthesis of emetine from the ester of N-[β-(3,4-dimethoxyphenyl)-ethyl)-β-ethyl-α-piperidone- γ-acetic acid (XIII), an intermediate compound of the product of condensation of the nitrile (X) (Z = –CN) with one molecule of homoveratrylamine (route B).

The prepared compounds (IX), whose structure was predetermined by the very mode of their synthesis, were proved to possess the structure of natural emetine on the basis of the following facts:

1. The synthetic emetines give all the color reactions characteristic of this alkaloid: a red color with the sodium salt of diazobenzene sulfonic acid; a green color with 1% solution of ammonium molybdate in sulfuric acid in presence of traces of hydrochloric acid (Frohde reagent); a yellowish-green color with sulfomolybdic acid.

2. The absorption curve of the prepared hydrochloride of d,l-emetine (m. pt. 145-146°) coincides with the absorption curve of natural emetine hydrochloride (Fig. 1).

3. Oxidation of the prepared bases with iodine gave one and the same substance which was completely identical with the rubremetine, formed by oxidation of natural emetine (Fig. 2). The rubremetine formed by the action of mild oxidizing agents (iron chloride [17], bromine [18], iodine [19], and mercuric acetate [20]) on the natural alkaloid, does not differ from the rubremetine prepared synthetically.

In view of the presence in the structural formula of emetine of four asymmetric carbon atoms (C_9, C_7, C_8, C_1') we may assume that the solid and liquid emetines isolated by us comprise a mixture of isomers due to the asymmetry at the C_1' atom in the isoquinoline nucleus and at the C_9 atom in the quinolizine nucleus. For the separation of the individual isomers we converted the obtained bases into various salts. From the solid isomer (m. pt. 60-63°) we succeeded in preparing the crystalline camphor-β-sulfonate, from which was isolated the base with m. pt. 71.5-72.5°. The d-tartarate of the latter (m. pt. 159-161.5°), also the base separated therefrom (m. pt. 71.5-72.5°), are completely identical with, respectively, the d-tartrate and the l-emetine of the natural product.

EXPERIMENTAL

1. Ethyl ester of acetone dicarboxylic acid (XV) is prepared by the usual method, e.g. from citric acid which is treated with concentrated sulfuric acid containing 20% sulfur trioxide followed by esterification of the resultant acetone dicarboxylic acid (92% yield) with ethyl alcohol in presence of hydrogen chloride. B. pt. 118-120° (2 mm), 125-127° (5 mm). Yield 45% of theory based on the citric acid.

The methyl ester of acetone dicarboxylic acid has b. pt. 131-135° at 10 mm. Yield 46% of theory.

2. Ethyl ester of β-hydroxyglutaric acid (XVI). 62 g ethyl acetone dicarboxylate in 20 ml absolute alcohol is hydrogenated in presence of 2 g skeletal nickel catalyst at an initial hydrogen pressure of 130 atm and at a temperature of 150° for 4 hours. After cooling, the catalyst is filtered off, the alcohol distilled off in vacuum, and the residue distilled. B. pt. 128-130° (5 mm). Yield 57.8 g or 92.5% of theory.

Methyl ester of β-hydroxyglutaric acid has b. pt. 138-139° at 8 mm. Yield 85% of theory.

3. Ethyl ester of β-acetoxyglutaric acid (XVII). 57.8 g (1 mole) ethyl β-hydroxyglutarate and 37 g (1.3 moles) freshly distilled acetic anhydride are heated for one hour with gentle boiling. The excess of acetic anhydride and acetic acid are distilled off in vacuum, and the residue is distilled. B. pt. 138-140° at 4 mm. Yield 67.2 g or 96.5% of theory.

Methyl ester of β-acetoxyglutaric acid has b. pt. 134-135° at 5 mm. Yield 95% of theory.

4. Ethyl ester of glutaconic acid (XVIII). 30 g (1 mole) ethyl β-acetoxyglutarate is heated with 0.1 g (0.0084 mole) fused potassium acetate until the acetic acid is distilled off, care being taken that the temperature of the vapor does not exceed 135°. At the end of the distillation potassium acetate comes down and the heating is then stopped. The cooled reaction mass is treated with absolute ether for complete removal of the substance from the potassium acetate. The ether is distilled off and the residue redistilled in vacuum. B. pt. 103-105° at 3 mm, 127-129° at 14 mm. Yield 16.9 g or 74.5% of theory. Dilution of the distilled acetic acid with water yields a further 1-1.5 g of glutaconic ester.

The methyl ester of glutaconic acid has b. pt. 94-95° at 2 mm. Yield 71.5%.

5. Ethyl ester of β-(α'-cyano-α'-carbethoxy)-methylglutaric acid (XIX). A mixture of 63 g (1 mole) freshly distilled ethyl glutarate, 88 g (2.3 moles) ethylcyanoacetate, 63 ml absolute ethyl alcohol and 20 drops sodium ethylate solution (the latter prepared from 3.6 g metallic sodium and 40 ml absolute alcohol) is kept at a gentle boil for 12 hours. Maintenance of the necessary alkaline reaction of the solution is ensured by the addition every two hours of 20 drops of sodium ethylate. After cooling, the alcohol is distilled off in vacuum and to the water is added 15 ml water. The separated oil is collected, the aqueous layer extracted with ether (benzene), the ethereal extract combined with the oil and the whole dried with ignited sodium sulfate. After removal of the solvent the residue is distilled in vacuum. B. pt. 167-169° at 3 mm. Yield 85 g or 84% of theory.

The methyl ester of β-(α'-cyano-α'-carbomethoxy)-methylglutaric acid has b. pt. 157-159° at 2 mm, 189-192° at 10 mm. Yield 74.5% of theory.

6. Ethyl ester of β-(α'-cyano-α'-carbethoxy)-propylglutaric acid (XX). To a solution of sodium ethylate prepared from 7.4 g (1.2 moles) metallic sodium and 148 ml absolute alcohol is added a mixture of 83 g (1 mole) ethyl ester of β-(α'-cyano-α'-carbethoxy)-methylglutaric acid and 92 g (2 moles) ethyl iodide. The reaction mass is kept at the boil until the reaction is neutral, which usually requires 3 hours. On cooling, the alcohol is distilled off in vacuum and to the residue is added 20 ml of water. The separated oil is removed, the aqueous layer is extracted with benzene. After the usual working up of the benzene extract (combined with the oil layer) and distillation of the solvent, the residue is distilled in vacuum. B. pt. 169-171° at 3 mm. Yield 82 g or 88.3% of theory.

d_{20}^{20} 1.0947; n_D^{20} 1.4521; MR_D 80.70; calculated 80.85.

3.035 mg substance: 6.545 mg CO_2; 2.080 mg H_2O; 5.945 mg substance: 0.245 ml N_2 (24°, 731 mm). Found %: C 58.81, H 7.66; N 4.5. $C_{16}H_{25}O_6N$. Calculated %: C 58.68; H 7.70; N 4.27.

The methyl ester of β-(α'-cyano-α'-carbethoxy)-propylglutaric acid is prepared similarly, by condensation of methyl glutaconate with methyl ethylcyanoacetate. The yield was lower. B. pt. 150-152° at 1 mm.

d_{20}^{20} 1.825; n_D^{20} 1.4597; MR_D 65.97. $C_{13}H_{19}O_6N$. Calculated: MR_D 65.75.

7. Ethyl ester of β-(α'-cyano)-propylglutaric acid (X, Z = —CN). To a solution of sodium alcoholate prepared from 1.81 g (1 mole) metallic sodium and 40 ml absolute ethyl alcohol is added 25.8 g (1 mole) ethyl ester of β-(α'-cyano-α'-carbethoxy)-propylglutaric acid (XX). The reaction mass turns yellow and thickens. Addition is then made of 1 42 g (1 mole) water and the mass left for 12 hours and then heated for an hour at the boil. The excess of alcohol is distilled off in vacuum and the residue dissolved in 15 ml of water. The solution is extracted with ether to remove the unsaponified tricarboxylic ester and then cooled before acidifying with hydrochloric acid. An oil separates and is carefully extracted with ether. After removing the ether from the dried extract, the residue is heated in a vacuum (15 mm) at 170-180° for one hour. The residue is cooled and dissolved in ether, and the solution well washed with sodium bicarbonate solution. After drying with magnesium sulfate, the ether is distilled off and the residue distilled in vacuum. B. pt. 139-140° at 2.5 mm. Yield 6 g or 30 % of theory.

d_{20}^{20} 1.0535; n_D^{20} 1.4519; MR_D 65.32; calculated 65.35.

3.320 mg substance: 7.430 mg CO_2; 2.460 mg H_2O. 3.170 mg substance: 7.130 mg CO_2; 2.310 mg H_2O. 5.110 mg substance: 0.254 ml N_2 (23°, 719 mm). 5.480 mg substance: 0.263 ml N_2 (22°, 728 mm). Found %: C 61.03, 61.34; H 8.29, 8.15; N 5.45, 5.31. $C_{28}H_{31}O_4N$. Calculated %: C 61.14; H 8.29; N 5.48.

8. β"-(3", 4"-Dimethoxyphenyl)-ethylamide-N-[β'-(3',4'-dimethoxyphenyl)]-ethyl-δ-ethyl-α-piperidone-γ-acetic acid — diamide (XI). A mixture of 5.2 g (1 mole) ethyl ester of β-(α'-cyano)-propylglutaric acid, 24 g (6.5 moles) homoveratrylamine, 8 g skeletal nickel catalyst and 15 ml absolute ethyl alcohol is heated in an autoclave at 110-115° and an initial hydrogen pressure of 130 atms for two hours. After cooling, the catalyst is filtered off. The alcohol is distilled off in vacuum, and the residue heated on an oil bath at 180-200° for three hours. The cooled reaction mass is rapidly and thoroughly washed with excess (200-300 ml) absolute ether in order to remove homoveratrylamine. The residue after removing the ether solution is a yellow, viscous oil soluble in alcohol and chloroform, insoluble in water, ether and benzene. It is a mixture of stereoisomeric diamides. Yield 9.0 g or 86% of theory.

7.450 mg substance: 0.358 ml N_2 (24°, 735 mm). Found %: N 5.34. $C_{39}H_{49}O_6N_3$. Calculated %: N 5.59.

The obtained mixture was resolved with the help of absolute toluene into two fractions: 3.2 g of isomer A, soluble in toluene, and 5.8 g of isomer B, insoluble in toluene. Further transformations were performed separately with each isomer.

9. Hydrochloride of 4', 5'-dimethoxy-6-ethyl-7-(1"-methyl-6", 7"-dimethoxy-3", 4"-dihydroisoquinolyl)-3, 4, 5, 6, 7, 8-hexahydro-9, 10-dehydro-(1,2:1',2')-benzquinolizine chloride (XII).

a) A mixture of 3.2 g isomer A of β"-(3", 4"-dimethoxyphenyl)-ethylamide-N-(β'-(3', 4'-dimethoxyphenyl-ethyl)-δ-ethyl-α-piperidone-γ-acetic acid, dissolved in 40 ml absolute toluene, and 25 ml freshly distilled phosphorus oxychloride is heated for an hour at a gentle boil. The toluene and excess phosphorus oxychloride are distilled off in vacuum. The residue is washed several times with absolute alcohol and then dissolved in 8 ml of 6 % hydrochloric acid. The solution is evaporated in vacuum to give 3.5 g of red-brown oil readily soluble in water, alcohol and chloroform, insoluble in ether and benzene.

b) A mixture of 5.8 g of isomer B of β"-(3", 4"-dimethoxyphenyl)-ethylamide-N-[β'-(3', 4'-dimethoxyphenyl)-ethyl]-δ-ethyl-α-piperidone-γ-acetic acid, suspended in 40 ml toluene, and 4.5 ml freshly distilled phosphorus oxychloride is heated for an hour at a gentle boil. Further treatment was as for isomer A. There was obtained 6.2 g red-brown oil. The latter was characterized by preparation of the corresponding hydroiodide of 4', 5'-dimethoxy-6-ethyl-7-(1"-methyl-6", 7"-dimethoxy-3", 4"-dihydroisoquinolyl)-3,4,5,6,7,8-hexahydro-9,10-dehydro-(1',2':1,2)-benzquinolizine iodide. To the aqueous solution of hydrochloride of the chloride (XII) is added an aqueous solution of sodium iodide until precipitation is complete. The iodide is extracted with chloroform and the extract dried with ignited magnesium sulfate. Distillation of the solvent leaves a yellow residue. The iodide is purified by dissolving in alcohol and precipitating with ether. The compound is slightly hygroscopic. After drying in a vacuum desiccator the m. pt. is 257-258°. Readily soluble in alcohol and chloroform, sparingly soluble in water, insoluble in ether and benzene.

3.150 mg substance: 5.510 mg CO_2; 1.620 mg H_2O. 3.255 mg substance: 5.710 mg CO_2; 1.660 mg H_2O. 8.380 mg substance: 0.314 ml N_2 (24°, 723.3 mm). Found %: C 47.71, 47.84; H 5.75, 5.71; N 4.09. $C_{29}H_{33}O_4N_2I_3$. Calculated %: C 47.52; H 5.23; N 3.82.

10. 4', 5'-Dimethoxy-6-ethyl-7-(1"-methyl-6",7"-dimethoxy-1", 2", 3", 4"-tetrahydroisoquinolyl)-3,4,5, 6, 7, 8, hexahydro-1,2:1', 2'-benzquinolizine — emetine bases (IX).

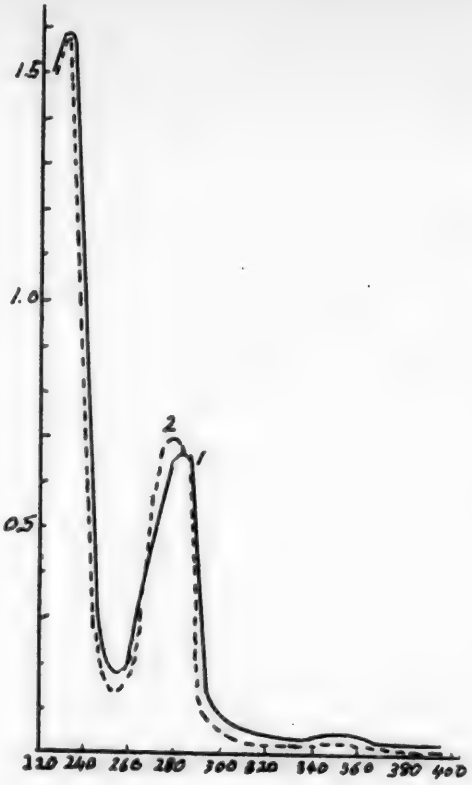


Fig. 1.
1 – Hydrochloride of natural emetine;
2 – hydrochloride of synthetic emetine.

a) 3.5 g of hydrochloride of the chloride (XII), prepared from the A isomer (XI), is treated in 10 ml absolute alcohol with alcoholic ammonia solution. The resultant precipitate is filtered, and the alcoholic filtrate is charged into an autoclave where it is hydrogenated in presence of 8 g skeletal nickel catalyst at 70-80° and an initial hydrogen pressure of 130 atm. for two hours. After cooling, the catalyst is removed, the alcohol distilled off in vacuum and the residue dissolved in 8 ml water. The aqueous solution is treated with ammonia while being cooled, and the separated oil is extracted with ether. The extract is washed with 5% alkali solution and dried with potassium carbonate. After removing the ether, a light-yellow oil remains. Yield 1.7 g or 55.5% of theory.

6.060 mg substance: 0.323 ml N_2 (22°, 741 mm). Found %: N 6.01. $C_{29}H_{40}O_4N_2$. Calculated %: N 5.89.

b) In a similar manner, 6.2 g of the hydrochloride of the chloride (XII), prepared from isomer B (XI), is converted (after distilling off the ether) into a yellow, amorphous substance with m. pt. 60-63°. Yield 1.0 g or 18.4% of theory.

When using platinum catalyst this process proceeds in the following manner: 4 g hy rochloride of chloride (XII), prepared from isomer B (XI), in 15 ml alcohol is hydrogenated in presence of 0.4 g platinum oxide at 1.5-2 atm. After 0.5 mole hydrogen has been taken up, which requires 30 minutes, the hydrogenation comes to a stop. The inactivated catalyst is filtered off, 0.2 g fresh platinum oxide is added, and hydrogenation is resumed at 130 atm., 1.5 moles hydrogen being then absorbed in 10-15 minutes. The solution, dark-red in color prior to hydrogenation, is light-yellow. Further treatment is as above. There is obtained a white, amorphous substance which turned yellow in the light. Yield 1.4 g or 40% of theory.

5.235 mg substance: 0.284 ml N_2 (25°, 740 mm). Found %: N 6.04. $C_{29}H_{40}O_4N_2$. Calculated %: N 5.89.

11. Emetine hydrochloride. a) It was not possible to isolate the crystalline hydrochloride of the emetine prepared from isomer A (XI).

b) The ethereal solution of the emetine base prepared from isomer B (XI), was saturated with an ethereal solution of hydrogen chloride to give a white powder with m. pt. 145-146° (beings to change at 100-102°). The substance is readily soluble in water and alcohol, insoluble in ether and benzene; it is hygroscopic. Prior to each analysis the preparation was dried in vacuum at 110° for 1½ hours.

3.110 mg substance: 7.205 mg CO_2; 2.140 mg H_2O. 4.845 mg substance: 0.225 ml N_2 (22°, 735 mm). 5.320 mg substance: 2.695 mg AgCl. Found %: C 63.18; H 7.70; N 5.2; Cl 12.55.

$C_{29}H_{40}O_4N_2 \cdot 2HCl$. Calculated %: C 62.89; H 7.48; N 5.06; Cl 12.83.

The absorption spectrum of the hydrochloride of synthetic emetine is identical with that of the hydrochloride of natural emetine (Fig. 1).

12. Rubremetine iodide. a) Oxidation of the synthetic emetine base obtained from isomer A diamide (XI). 0.5 g base, 20 ml ethyl alcohol and 1 g iodine are heated for 3 hours on the water bath and for 45 minutes on the oil bath at 140-145°. The reaction mass, after cooling, is poured into sodium becarbonate solution. A brown precipitate is formed. This is drained, washed with water and recrystallized from a mixture of acetone and water. M.p. 178.5-181°. Yield 0.08 g or 12.8% of theory.

3.150 mg substance: 6.685 mg CO_2; 1.600 mg H_2O. 6.060 mg substance: 0.240 ml N_2 (23°, 752 mm). Found %: C 57.88; H 5.68; N 4.52. $C_{29}H_{33}O_4N_2I$. Calculated %: C 58.0; H 5.54; N 4.65.

b) Oxidation of synthetic emetine base prepared from the diamide of isomer B (XI). 0.5 g emetine base, 20 ml ethyl alcohol and 1 g iodine are heated under a reflux condenser for 3½ hours. The reaction mass is treated as in a). Rubremetine iodide separates in the form of orange-red crystals. M. pt. 178-181°. Yield 0.12 g, 19.2% of theory.

3.185 mg substance: 6.765 mg CO_2; 1.555 mg H_2O. 6.335 mg substance: 0.264 ml N_2 (25°, 752 mm). Found %: C 57.93; H 5.46; N 4.72. $C_{29}H_{33}O_4N_2I$. Calculated %: C 58.0; H 5.54; N 4.65.

c) Oxidation of natural emetine base. Heating of a mixture of 0.5 g natural l-emetine with 1 g of iodine in alcoholic solution under the conditions described for conversion of the synthetic emetines into rubremetine iodide gives 0.15 g rubremetine iodide (24% of theory).

The prepared rubremetine iodide melts at 177-179°. The mixed samples of rubremetine iodide prepared from natural emetine with the rubremetine iodides prepared from synthetic emetines did not exhibit a depression. The absorption spectra of the prepared rubremetine iodides coincide completely (Fig. 2).

13. Camphor-β-sulfonate of natural l-emetine. 0.177 g (1 mole) natural l-emetine base is dissolved in absolute alcohol and addition is made of 0.170 g (2 moles) of d,l-camphor-β-sulfonic acid and a few drops of absolute ether. A precipitate comes down on standing and is filtered off and washed with absolute alcohol and ether. There is obtained 0.1723 g camphor-β-sulfonate of l-emetine with m. pt. 210-213°. After recrystallization from absolute alcohol the yield is 0.0943 g or 27.1% of theory. M. pt. 222-223°.

3.150 mg substance: 7.210 mg CO_2; 2.075 mg H_2O. 3.050 mg substance: 6.950 mg CO_2; 2.085 mg H_2O. 5.565 mg substance: 0.147 ml N_2 (24°, 746 mm). 5.295 mg substance: 0.150 ml N_2 (23°, 743 mm). Found %: C 62.42, 62.14; H 7.37, 7.65; N 2.98, 3.19. $C_{29}H_{40}O_4N_2 \cdot 2C_{10}H_{16}O_4S$. Calculated %: C 62.25; H 7.68; N 2.96.

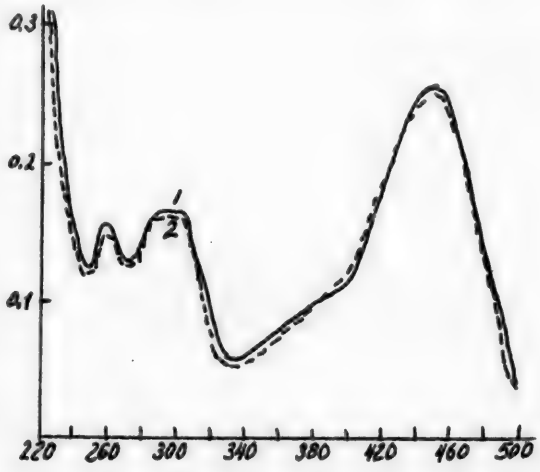


Fig. 2.
1 – Rubremetine iodide prepared from natural emetine;
2 – rebremetine iodide prepared from synthetic emetine.

14. Camphor-β-sulfonate of synthetic emetine. a) 1.033 g (1 mole) emetine base with m. pt. 60-63°, prepared from B-isomer diamide (XI), is dissolved in 5 ml absolute alcohol and addition is made of 0.996 g (2 moles) d,l-camphor-β-sulfonic acid. On introducing a seed of the camphor-β-sulfonate of natural emetine, a precipitate gradually comes down. The salt is filtered off and washed with absolute alcohol and ether. There is obtained 0.2392 g (12% of the theoretical yield) of emetine camphor-β-sulfonate with m. pt. 225-227.5°. Recrystallization from absolute alcohol gave 0.212 g (10.4% of the theoretical yield). M. pt. 238.5-240°.

3.005 mg substance: 6.870 mg CO_2; 2.040 mg H_2O. 2.990 mg substance: 6.850 mg CO_2; 2.070 mg H_2O. 5.055 mg substance: 0.119 ml N_2 (22°, 748 mm). 7.20 mg substance: 0.171 ml N_2 (25°, 745.4 mm). Found %: C 62.35, 62.48; H 7.59, 7.75; N 2.68, 2.67. $C_{29}H_{40}O_4N_2 \cdot 2C_{10}H_{16}O_4S$. Calculated %: C 62.25; H 7.68; N 2.96.

b) The emetine base prepared from isomer A diamide (XI) does not form crystalline products with camphor-β-sulfonic acid. A substance identical with that described above could only be isolated in a small yield.

15. Isolation of emetine base from emetine camphor-β-sulfonate. a) Synthetic emetine. 0.158 g camphor-β-sulfonate of synthetic emetine with m. pt. 238.5-240° is dissolved in 12 ml water and treated with 10% sodium hydroxide solution. The resultant precipitate of emetine base is filtered and washed with water. M. pt. 71.5-72.5°. Yield 0.056 g, 69.7% of theory. Emetine base was obtained in the form of a white amorphous powder,

readily soluble in methyl and ethyl alcohols, ether, acetone and chloroform, less easily soluble in carbon tetrachloride, petroleum, ether and benzene, sparingly soluble in water.

3.010 mg substance: 7.980 mg CO_2; 2.120 mg H_2O. Found %: C 72.30; H 7.88. $C_{29}H_{40}O_4N_2$. Calculated %: C 72.45; H 8.39.

b) l-Emetine (natural). From 0.15 g natural emetine camphor-β-sulfonate is obtained l-emetine base with m. pt. 71.5-72.5°. Yield 0.05 g, 65.6% of theory.

3.025 mg substance: 8.010 mg CO_2; 2.100 mg H_2O. Found %: C 72.33; H 7.78. $C_{29}H_{40}O_4N_2$. Calculated %: C 72.45; H 8.39

No depression was observed in a mixed melting point determination on synthetic and natural emetines.

16. Emetine hydrochloride. To an ethereal solution of synthetic emetine base is added a saturated ethereal solution of hydrogen chloride. The resultant precipitate of emetine hydrochloride is washed several times with absolute ether. It forms a white powder with m. pt. 243-255°. The hydrochloride prepared from natural emetine has m. pt. 235-255°. Prior to each analysis the preparation is dried in vacuum at 110° for 1½ hours.

3.080 mg substance: 7.110 mg CO_2; 2.045 mg H_2O. 6.000 mg substance: 0.289 ml N_2 (23°, 727 mm). 5.950 mg substance: 3.025 mg AgCl. Found %: C 62.96; H 7.43; N 5.31; Cl 12.58.

$C_{29}H_{40}O_4N_2 \cdot 2HCl$. Calculated %: C 62.89; H 7.48; N 5.06; Cl 12.83.

SUMMARY

For the first time a complete synthesis of the alkaloid, emetine, has been realized. It has confirmed its structure as 4', 5'-dimethoxy-6-ethyl-7-(1''-methyl-6'', 7''-dimethoxy-1'', 2'', 3'', 4''-tetrahydroisoquinolyl)-3,4,5,6,7,8,-hexahydro-1,2:1',2'-benzquinolizine.

LITERATURE CITED

[1] Pelletier, J. Pharm., 3, 147; 4, 322 (1817).

[2] V. Podvysotsky, New Pharmaceutical and Chemical Investigations of the Alkaloids of the Ipecacuanha Root, Emetine (1879).

[3] Pelletier, Dumas, Ann. Chim. Phys., 2 (14), 180 (1823); Reich. Arch. Pharm., 163, 208 (1863); Wurtz, M J. Lefort, Ann. Chim. Phys., 5 (8), 277 (1877); H. Kunz, Arch. Pharm., 225, 461 (1887); A. Windaus, L. Herrmans, Ber., 47, 1470 (1914); C. Hesse, . . Ann., 405, 1 (1914); P. Karrer, Ber., 49, 2057 (1916).

[4] E. Spath, W. Leithe, Ber., 60, 688 (1927).

[5] H. Staub, Helv. Chim. Acta, 10, 826 (1927).

[6] R. Robinson, J. Chem. Soc., 1927, 1067.

[7] W. H. Brindley, F. L. Pyman, J. Chem. Soc., 1927, 1067.

[8] E. Spath, M. Pailer, Monatsh., 78, 348 (1948); M. Pailer, Monatsh., 79, 127 (1948); 80, 94 (1949); M. M. Janot, Bull. Soc. Chim., 1949, 185; A. R. Battersby, H. T. Openshaw, J. Chem. Soc., Suppl., No. 159 (1949); J. Chem. Soc., 1949, 3207; A. R. Battersby, H. T. Openshaw, H. C. G. Wood, Experientia 5, 114 (1949); C. A., 43, 7492 (1949).

[9] R. S. Livshits, N. A. Preobrazhensky and M. S. Bardinskava, J. Gen. Chem., 15, 836 (1945).

[10] R. Robinson, Nature, 162, No. 524, 155 (1948); M. M. Janot, Bull. Soc., Chim., 1949, 185.

[11] Organic Syntheses, I, 70, 536 (1949).

[12] H. L. Lochte, P. L. Pickard, J. Am. Chem. Soc., 68, 721 (1946); M. Marcel, Delepine, C. r., 224, 1396 (1947).

[13] B. S. Gidvani, J. Chem. Soc., 1932, 2666; G.A.R. Kon, K.S. Nargung, J. Chem. Soc., 1932, 2462; Blaise, Bull.Soc.chim.de France, (3) 29, 1014.

[14] E. P. Kohler, C.H. Reid, J. Am.Chem.Soc., 47, 2803 (1925).

[15] F. F. Blicke, W.B. Wrigt, M.F. Zienty, J.Am.Chem.Soc., 63, 1964 (1941); K. Kindler, F. Hesse, Arch. Pharm., 271, 439 (1933); H.J.Schweglen and H.Adkins. J.Am.Chem.Soc., 61, 3499 (1939); S.W.Hoerr, J.Org.Chem., 9, 201 (1944); B.S.Biggs and W.S.Bishop. Ind.Eng.Chem., 38, 1084 (1946); H.Henecke. Ber., 82, 104 (1946); W.B.Martin and A.E.Manteil. J.Am.Chem.Soc., 70, 1817 (1948).

[16] On the stereochemistry of quinoline alkaloids, see V.Prelog et al. Helv.Chim.Acta, 27, 535, 545 (1944); 33, 164, 2021 (1950).

[17] F.L.Pyman. and F.H.Carr. J.Chem.Soc., 104, 1591 (1914). . . . , ,).

[18] F.L.Pyman. J.Chem.Soc., 111, 419 (1917); H.Staub. Helv.Chim.Acta, 10, 826 (1927).

[19] P.Karrer. Ber., 50, 582 (1917); F.L.Pyman. J.Chem.Soc., 113, 222 (1918).

[20] A.R.Battersby and H.T.Openshaw. J.Chem.Soc., Suppl.No.1, 67 (1949).

Received May 25, 1951

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Determination of the Mixed Sulfates of the Alkali Elements and Ammonium.

(Viktor I. Spitsyn and M. A. Meerov. p. 1327)

Crystals of cesium-ammonium sulfate (X 10).

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